ABSORPTION
OF
NITROUS GASES

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PREFACE

In peace and war alike the supply of fixed nitrogen is of vital importance to the existence of the nation. In almost all processes for the fixation of nitrogen the production of oxides of nitrogen is one of the fundamental intermediate stages. It cannot be said at the present time, however, that the problem of the technical utilization of nitrous gases (which are usually largely diluted with air) has met with a satisfactory solution. The enormous number of patents relating to the process which appear each year would seem to be sufficient evidence of the truth of this statement. It is the common practice at the present time to absorb the nitrous gases in water with the production of dilute nitric acid, which acid is either concentrated or converted into solid nitrates. In this country, where nitrous gases are produced (in the majority of cases) only as a by-product, the chemical principles underlying the process have not been studied to a very great extent, and it is very often the case that the absorption process is conducted on rule-of-thumb methods. While the loss of fixed nitrogen in such plants may not be a very serious factor in the series of industrial operations with which it is connected, the same view cannot possibly be held when the recovery of the nitrous gases is one of the main objects of those industrial operations. Furthermore, it has long been evident that we, in this country, must ultimately adopt some process for the fixation of nitrogen, in view of the fact that we import nearly all our fertilizers.

With these points in view, the author has endeavoured to discuss the absorption of nitrous gases in water, both from a theoretical and an industrial standpoint. The most important types of absorption processes, other than water absorption, which have been developed are also considered, and an attempt has been made to classify and compare them, in order to

survey the present position, so far as this particular branch of the nitrogen-fixation industry is concerned. It has also been thought necessary to review briefly the methods available for the commercial utilization of the dilute nitric acid normally obtained from the water-absorption process.

Such methods include the concentration of the acid, and also its conversion into solid nitrates. The handling and measurement of gases have been dealt with in some detail and the problem of pumping dilute acids has also been discussed. It was felt that the volume would not be complete without detailed reference to the approximate and accurate analytical methods which might be necessary in the control of absorption plant in general.

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CHAPTER 1

OXIDES AND OXYACIDS OF NITROGEN

As a preliminary to a consideration of the absorption of nitrous gases, it is necessary to review briefly the more important properties of the substances commonly dealt with in absorption practice. While the description given does not aim at being exhaustive, either as regards the chemical properties of the substances mentioned, or in the number of compounds included for discussion, it is an attempt to indicate the chief reactions which may have a bearing on modern absorption practice. For this reason, although many of its compounds are dealt with, an account of gaseous nitrogen is deemed of insufficient direct importance for inclusion in this chapter. Nor also have substances such as calcium, sodium and ammonium nitrates and nitrites been included, although there is some argument in favour of their introduction, since they are often the ultimate product obtained from an absorption system. A detailed discussion of the methods of manufacture of ammonium or calcium nitrate from dilute nitric acid, however, is considered to be rather outside the scope of this work.

The Oxides of Nitrogen

Nitrous Oxide, N_2O

Preparation. This gas is obtained in small quantities when certain substances which are easily oxidized are acted upon by nitric oxide [NO],[1] for example, potassium sulphite, moist iron filings, zinc filings, and stannous chloride.

It is also formed by the action of sulphur dioxide on nitric oxide, and by dissolving metallic zinc in very dilute nitric acid.[2]

[1] Priestley, 1772. [2] Lunge, *Ber.*, 1881, **14**, 2106.

Nitrous oxide is one of the reduction products of nitrates, nitrites, and nitrous acid, e.g., platinum black and sodium amalgam quite readily reduce nitrites and nitrous acid to nitrous oxide.

The gas has also been detected in the non-condensible gases obtained in the preparation of nitric acid from sodium nitrate and sulphuric acid, and in the nitrous gases evolved during the denitration of waste acid from the manufacture of explosives.

The best methods of preparation are as follows :—

1. By heating ammonium nitrate.

$$NH_4NO_3 = N_2O + 2H_2O.$$

The decomposition begins about 170° C. and the temperature then requires careful regulation, and should not rise above 260° C., or the reaction becomes explosive, particularly if the ammonium nitrate layer is fairly thick. The gas obtained is liable to contain nitric oxide, nitrogen and chlorine (from the ammonium chloride commonly present as impurity in the nitrate). If too high a temperature is used, nitrogen tetroxide is also present. Organic matter should also be absent, or carbon dioxide will form an additional impurity in the gas.

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To purify nitrous oxide, it is usual to pass the gas through a concentrated solution of ferrous sulphate, then through a dilute solution of caustic soda, and finally through concentrated sulphuric acid to dry it.

Lidoff [1] recommends that the gas should be passed through a solution of ferrous sulphate, and then an emulsion of ferrous sulphate in concentrated sulphuric acid. He also states that the preparation of nitrous oxide may be effectively carried out by heating at 260°–285° C. a mixture of two parts of ammonium nitrate (dried at 105° C.) with three parts of dry sand.

2. W. Smith [2] recommends the use of an equimolecular mixture of sodium nitrate and ammonium sulphate (not chloride) heated at a temperature of 240° C., whereby a regular evolution of nitrous oxide takes place. The method is also described and patented by Thilo.[3]

[1] *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 59.
[2] *J. Soc. Chem. Ind.*, 1892, **11**, 867.
[3] *Chem. Zeit.*, 1894, **18**, 532.

3. Quartaroli [1] obtains nitrous oxide by warming a nitrate with anhydrous formic acid. As carbon dioxide is simultaneously evolved the gas is collected over 20 per cent. caustic potash solution.

$$2KNO_3 + 6H{\cdot}COOH = N_2O + 4CO_2 + 2H{\cdot}COOK + 5H_2O.$$

4. Nitrous oxide is also obtained by warming a solution containing sodium nitrite and hydroxylamine hydrochloride.[2]

$$NH_2OH + HNO_2 = N_2O + 2H_2O.$$

5. Mixed with carbon dioxide, nitrous oxide is obtained by treating a solution of potassium nitrate (to which sulphuric acid is added until the solution contains about 20 per cent. H_2SO_4) with oxalic acid.[3]

$$4H_2C_2O_4 + 2KNO_3 + H_2SO_4 = 5H_2O + K_2SO_4 + 8CO_2 + N_2O.$$

6. The gas may also be prepared by the reduction of nitrous acid by means of hydrazine as described by Francke.[4]

$$N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O.$$

7. Nitrous oxide is evolved on heating a mixture of 5 parts of stannous chloride, 10 parts of concentrated hydrochloric acid (sp. gr. 1·21), and 0·9 parts of nitric acid (sp. gr. 1·38). Proportions other than the above are liable to give irregular and explosive evolution of the gas.

8. Pictet [5] and Södermann [6] state that at a definite point in the nitrogen-oxygen flame, the chief product is nitrous oxide, which may be obtained in 25 per cent. yield by rapid cooling.

Properties. The best method of obtaining the gas in a high degree of purity is to liquefy it and allow any accompanying nitrogen, together with a little of the nitrous oxide, to boil off.[7]

Critical temperature and pressure.

36·50° C. and 71·56 atmos.[8]
36·4° C. and 73·07 atmos.[9]
35·4° C. and 75·0 atmos.[10]

[1] *Gazzetta*, 1911, **41**, ii, 53. [2] Pollak, *Annalen*, 1875, **175**, 141.
[3] Desbourdeaux, *Compt. rend.*, 1903, **136**, 1068.
[4] *Ber.*, 1905, **38**, 4102. [5] Fr. Pat. 415,594, 1910.
[6] Fr. Pat. 411,785, 1910.
[7] Villard, *Compt. rend.*, 1894, **118**, 1096.
[8] Cardossi and Arni, *J. Chim. Phys.*, 1912, **10**, 504.
[9] Cailletet and Matthias. [10] Dewar, *Phil. Mag.*, 1884, [V.], **18**, 210.

Density (air = 1) = 1·5297.[1]

Weight of one litre = 1·9777.[2]

Nitrous oxide is an endothermic compound $[N_2][O] = -21{,}700$ cal. It is consequently decomposed by shock, e.g., the explosion of mercury fulminate.

Solubility. The solubility of nitrous oxide water is as follows [3]:—

Temp.	Solubility in c.c. N_2O (0° C. and 760 mm.) per c.c. water, determined at a pressure of 760 mm.
5° C.	1·048
10° C.	0·8878
15° C.	0·7377
20° C.	0·6294
25° C.	0·5443

Nitrous oxide is more soluble in ethyl alcohol than in water, the coefficient of absorption in alcohol being approximately 4·178 at 0° C., as compared with 1·305 in water at 0° C.[4]

On heating, nitrous oxide is decomposed into its elements. Hunter [5] finds the decomposition to be bi-molecular.

$$2N_2O = 2N_2 + O_2.$$

At 500° C. about 1·5 per cent. of the gas is decomposed, but the decomposition is practically complete at 900° C. Nitrous oxide, in consequence, will support the combustion of substances which are burning with sufficient vigour to start its decomposition, e.g., phosphorus, sulphur, carbon, etc.

It is readily reduced by hydrogen in the presence of platinum black, finely divided palladium, or reduced nickel, and this fact offers a method for its estimation.[6]

Hempel [7] analyses the gas by explosion with hydrogen.

Most metals yield peroxides when gently heated in the gas; but by further action of the heated peroxide, nitrites and nitrates are produced, e.g.,

$$Na_2O_2 + 2N_2O = 2NaNO_2 + N_2.$$

The gas is quantitatively decomposed by passing it over

[1] Rayleigh, *Proc. Roy. Soc.*, 1905, **74**, 406. [2] *Ibid.*
[3] Geffchen, *Zeitsch. physikal. Chem.*, 1904, **49**, 257.
[4] Carius, *Annalen*, 1855, **94**, 139.
[5] *Zeitsch. physikal. Chem.*, 1905, **53**, 441.
[6] Drehschmidt, *Ber.*, 1888, **21**, 3242.
[7] *Zeitsch. Elektrochem.*, 1906, **12**, 600.

heated copper. At temperatures below 350° C., cuprous oxide and not cupric oxide is formed by this reaction, showing that nitrous oxide at lower temperatures acts less vigorously as an oxidizing agent than does oxygen.[1]

Nitrous oxide is a valuable anæsthetic for some minor operations. The purification of the gas for use as an anæsthetic is discussed by Baskerville and Stevenson.[2]

Nitrous oxide is theoretically the anhydride of hyponitrous acid [$H_2N_2O_2$], but the acid is not formed by the solution of nitrous oxide in water.

The gas appears in absorption practice as a constituent of the gases from nitric acid manufacture, and also from the denitration of waste acids. Its presence does not interfere with the ordinary absorption processes, especially as it is usually present only in small concentration.

Nitric Oxide [NO]

Preparation. This oxide is generally considered to be the first oxidation product of nitrogen at high temperatures, but Pictet[3] states that nitrous oxide can be detected spectroscopically in the flame, at an earlier stage than can nitric oxide, and furthermore can be isolated from the flame in fair yield.

Nitric oxide is produced under most circumstances where nitrogen and oxygen are in contact at sufficiently high temperatures. The earliest observation that the two elements were capable of combination was due to Priestley in 1784, who found that slow combination occurred on sparking a mixture of the gases continuously, a result which was confirmed by Cavendish in 1785. Cavendish also showed that the combustion of hydrogen in excess of air gave water containing nitric acid.

The combination of nitrogen and oxygen in the electric arc was further studied by Sir W. Crookes in 1892, and by Lord Rayleigh in 1897, and the conditions under which the greatest efficiency is obtainable have been studied by Haber and his co-workers.[4]

[1] Holt and Sims, *Chem. Soc. Trans.*, 1894, **65**, 428.
[2] *J. Ind. Eng. Chem.*, 1911, **3**, 579. [3] Fr. Pat. 415,594, 1910.
[4] *Zeitsch. Elektrochem.*, 1910, **16**, 810; reference to earlier papers will also be found in this paper.

Wolokitin[1] states that no nitric oxide is produced at ordinary pressures when hydrogen burns in air, but at a pressure of 20 atmos. approximately 0·3 mols. of nitric oxide per 100 mols. of water are produced.

If the hydrogen is burned in an equimolecular mixture of nitrogen and oxygen, at a pressure of 15 atmos., 3 mols. of nitric oxide per 100 mols. water are produced.

Fischer and Braemar[2] showed that when hydrogen, carbon monoxide, acetylene, etc., are burned under liquid air, nitrogen trioxide may be detected.

Haber and others[3] have shown that nitric oxide can be detected in the carbon monoxide flame (the temperature of which lies between 2,600° and 2,670° C.). Increase of pressure up to nine atmospheres appears to increase the yield of nitric oxide, but the effect of further increase of pressure up to 45 atmos. offers no advantages. The use of temperatures attained by surface combustion for the production of nitric oxide has been described.[4]

Herman[5] describes the use of temperatures obtained by the surface combustion of methane, using a zirconia refractory. A yield of 3–4 per cent. by volume of oxides of nitrogen was obtained with a consumption of 2·5 cub. metres of methane per kilo HNO_3 (as 100 per cent.).

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Bender[6] uses an apparatus for the continuous production of oxides of nitrogen from gaseous mixtures containing nitrogen and oxygen, by burning under pressure fuels which form large quantities of water during combustion. The air is supplied in such quantities, and the velocity of the gases in the combustion chamber so regulated, that with an excess of oxygen of 7–10 per cent. the combustion gases contain 11–14 per cent. by volume of carbon dioxide.

Phillips and Bulteel[7] describe an apparatus in which air, or a mixture of oxygen and nitrogen, is drawn over the surface of that portion of a gas flame in which combustion is sub-

[1] *Zeitsch. Elektrochem.*, 1910, **16**, 814.
[2] *Ber.*, 1906, **39**, 940.
[3] *Zeitsch. physikal. Chem.*, 1909, **66**, 181; **67**, 343.
[4] Eng. Pats. 3,194, 26,499, 1913.
[5] D.R.P. 281,089, 1913.
[6] D.R.P. 258,935, 1912; *J. Soc. Chem. Ind.*, 1913, **32**, 656.
[7] Eng. Pat. 27,558 and 29,893, 1910; U.S.A. Pat. 1,035,732, 1912; *J. Soc. Chem. Ind.*, 1911, **30**, 1211.

stantially complete, the velocity of the air current being greater than that of the flame gases. The flame is preferably spread out so as to form a larger surface.

In order to obtain a higher yield of nitric oxide, many processes have been described for heating the nitrogen and oxygen together under high pressures. One method of carrying this out is by utilizing explosion pressures.

Häusser [1] explodes coal gas and air under pressure, and maintains the explosion pressure as long as possible. The products contain in this case 1·3–1·7 per cent. of nitric oxide.

Haber [2] states that when a flame is burnt under 8–10 atmospheres pressure, oxides of nitrogen are produced, and a 10 per cent. solution of nitric acid may be obtained by burning hydrogen in an equimolecular mixture of oxygen and nitrogen.

The question of the production of oxides of nitrogen in explosions in which excess of air is present is discussed by Dobbelstein,[3] and in particular the use of coke oven gas for this purpose.

Using an illuminating gas of the following composition,

H_2 = 44%	N_2 = 1%
CH_4 = 25%	O_2 = 8%
CO = 14%	Unsatd. hydrocarbons = 4%
CO_2 = 3%	

he obtained a yield of 125 grams of nitric acid per cub. metre at 5 atmos. pressure.

Increase in the yield of nitric oxide can be effected in two ways :—

(*a*) By increase in pressure.

(*b*) By increase in the proportion of oxygen up to the theoretical value required for nitric oxide.

The oxidation of nitrogen has also been successfully attempted by the use of catalysts, e.g. the calcined oxides of such metals as cobalt, chromium, nickel, platinum, palladium, barium, magnesium, lead, etc.

The action of the electric arc, hot flames, etc., is usually considered to be purely thermal, but Warburg [4] and others

[1] Fr. Pat. 420,112, 1910 ; *J. Soc. Chem. Ind.*, 1911, **30**, 360.
[2] *Zeitsch. angew. Chem.*, 1910, **23**, 684.
[3] *Stahl u. Eisen*, 1912, **32**, 1571 ; *J. Soc. Chem. Ind.*, 1912, **31**, 981.
[4] *Zeitsch. Elektrochem.*, 1906, **12**, 540.

have shown that nitric oxide is produced by the silent electric discharge, which suggests the possibility that the kinetic energy of the gases in the ordinary electric arc may be directly used up in the formation of nitric oxide, before the thermal equilibrium is established.

Nernst [1] has determined the concentration of nitric oxide at various temperatures in the equilibrium mixture.

TABLE 1

Temp. Deg. Absolute.	Volume per cent. NO observed.	Volume per cent. NO calculated.
1,811	0·37	0·35
1,877	0·42	0·43
2,033	0·64	0·67
2,195	0·97	0·98
2,580	2·05	2·02
2,675	2·23	2·35
3,200	5·0 (approx.)	4·39

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Nitric oxide is not stable above 1,200° C. and consequently the gases must be rapidly cooled in all processes where high temperatures are used to effect the union of nitrogen and oxygen. This is normally carried out by sweeping the gases rapidly out of the hot region, or in the case of the arc process, which is the only present successful thermal process, by making and breaking the arc several thousand times a second, or by using very thin and elongated arcs.

Jellinek [2] finds that nitric oxide decomposes at a measurable rate, even at 670° C., and also that both platinum and iridium act as catalysts in this decomposition, their catalytic activity decreasing with rise in temperature. The effect of platinum in this respect is important, as platinum net catalysts are used for the oxidation of ammonia to oxides of nitrogen.

Nitric oxide can also be produced by the action of a number of reducing agents on nitric and nitrous acids. The most convenient methods of preparation of the gas on a small scale are as follows :—

[1] *Zeitsch. anorg. Chem.*, 1906, **49**, 213.
[2] *Zeitsch. anorg. Chem.*, 1906, **49**, 229.

Preparation. 1. By the action of nitric acid of sp. gr. 1·2 on metallic copper.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

The gaseous impurities commonly present when the gas is prepared in this way are nitrogen and nitrous oxide. The quantity of nitrous oxide is found to increase as the amount of cupric nitrate in the solution increases.[1]

The preparation may be modified to give a purer nitric oxide by dropping nitric acid on to a column of copper turnings, and providing means for the removal of the copper nitrate at the base of the column. In any case, it is advisable to wash the gas so obtained with water, and lead it into a solution of ferrous sulphate or chloride, and afterwards regenerate by heating.

2. Nitric oxide may be prepared in a greater state of purity by heating ferrous sulphate with nitric acid, or alternatively by the action of sodium or potassium nitrate on a solution of ferrous sulphate in sulphuric acid, or preferably a solution of ferrous chloride in hydrochloric acid.[2]

$$6FeCl_2 + 2NaNO_3 + 8HCl = 6FeCl_3 + 2NaCl + 4H_2O + 2NO.$$

3. A similar method of preparing the gas is to allow a concentrated solution of sodium nitrite to drop into a solution of ferrous sulphate in sulphuric acid, or ferrous chloride in hydrochloric acid.[3]

$$HNO_2 + FeCl_2 + HCl = FeCl_3 + NO + H_2O.$$

4. Nitric oxide is slowly evolved when a mixture of potassium nitrite and ferrocyanide is dropped into dilute acetic acid and well shaken.[4]

$$K_4Fe(CN)_6 + HNO_2 + CH_3{\cdot}COOH = K_3Fe(CN)_6 + CH_3{\cdot}COOK + H_2O + NO.$$

5. Nitric oxide may also be prepared in a pure condition by shaking a solution of nitric acid in excess of concentrated sulphuric acid with mercury as in the ordinary nitrometer estimation.[5]

[1] Ackworth, *Chem. Soc. Trans.*, 1875, **28**, 828.
[2] Gay-Lussac, *Ann. Chim. Phys.*, 1847, [iii.], **23**, 203.
[3] Thiele, *Annalen*, 1889, **253**, 246.
[4] Deventer, *Ber.*, 1893, **26**, 589. [5] Emich, *Monatsh.*, 1892, **13**, 73.

6. When sulphuric acid (1 : 1) is dropped on a mixture of potassium iodide and potassium nitrite in the proportion of 1 part KI : 2 parts KNO_2, or alternatively by the interaction of hydriodic acid and nitrous acid, nitric oxide may be obtained in a very pure state.[1]

$$2HNO_2 + 2HI = 2H_2O + I_2 + 2NO.$$

7. Nitric oxide may also be prepared by passing sulphur dioxide into warm nitric acid of sp. gr. 1·15.[2]

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$

8. Nitric oxide is obtained in a pure state by heating some of the aromatic nitroso-compounds.[3] In particular a supply of pure gas is readily obtained by heating nitroso-diphenylamine *in vacuo* at 40°–75° C.,[4] or alternatively, if the dry substance is heated on an oil bath, at a temperature of 180°–190° C., nitric oxide of 99·7 per cent. purity is obtained.

9. A patent has been taken out for the production of nitric oxide by the electrolysis of a mixture of nitrous and nitric acid.[5] The concentration of nitric acid used is 20–30 per cent. HNO_3, containing 1–2 per cent. of nitrous acid, and a current of 5–10 amps. is used. The temperature should be below 50° C. or nitrogen tetroxide will be produced.

A similar process is described in Eng. Pat. 10,522, 1911, by which nitric oxide of 99–100 per cent. purity is obtained by electrolysing a solution containing not more than 40 per cent. HNO_3 and not more than 1 per cent. of HNO_2, at a temperature of 40°–50° C. The cathode may be of graphite, platinum, or gold.

While experience is not yet available concerning these electrolytic processes, the two methods recommended by Moser[6] as giving the purest nitric oxide are methods Nos. 5 and 6 ; but in the author's opinion the method of Marqueyrol and Florentin (method No. 8) gives the purest NO obtainable.

Properties. Nitric oxide is a colourless gas which is liquefied with difficulty to a colourless liquid.

[1] Winkler, *Ber.*, 1901, **34**, 1408.
[2] Weber, *Pogg. Ann.*, 1867, **130**, 277.
[3] Wieland, *Annalen*, 1911, **381**, 200.
[4] Marqueyrol and Florentin, *Bull. Soc. Chim.*, **1913**, **13**, 69.
[5] D.R.P. 244,362, 1912.
[6] *Zeitsch. anal. Chem.*, 1911, **50**, 401.

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Density	= 1·0387.
Weight of one litre at N.T.P.	= 1·3402 grm.
Critical temperature	= − 92·9°.
Critical pressure	= 64·6 atmos.[1]
Boiling-point of liquid NO	= 150·2°.
Solidifying-point	= − 160·6°.

Nitric oxide is slightly soluble in water. The absorption coefficient for various temperatures has been determined by Winkler.[2]

TABLE 2

Deg. Cent.	Absorption Coefft.	Deg. Cent.	Absorption Coefft.
0	0·07381	40	0·03507
5	0·06461	50	0·03152
10	0·05709	60	0·02954
15	0·05147	70	0·02810
20	0·04706	80	0·02700
25	0·04323	90	0·02648
30	0·04004	100	0·02628

Nitric oxide is also soluble in sulphuric acid, a fact which is sometimes overlooked in the use of the Lunge nitrometer for the estimation of nitric acid, nitrates, etc.

Lunge [3] states that 10 c.c. of 96 per cent. sulphuric acid will dissolve 0·35 c.c. of nitric oxide at 18° C. and 760 mm. Lubarsch [4] gives the following figures of absorption by 100 volumes of sulphuric acid.

	Per cent. H_2SO_4.	Vols. NO per 100 vols. Sulphuric Acid.
Monohydrate. . . .	100	3·5
$H_2SO_4 + 2{\cdot}5H_2O$ . .	68·5	1·7
$H_2SO_4 + 6{\cdot}5H_2O$ . .	45·5	2·0
$H_2SO_4 + 9H_2O$ . . .	37·7	2·7
$H_2SO_4 + 17H_2O$ . . .	24·3	4·5
Pure water . . .	—	7·2

On the other hand, Tower [5] finds that for sulphuric acid of

[1] Adwentowski, *Chem. Soc. Abstr.*, 1910, ii, 199.
[2] *Ber.*, 1901, **34**, 1408.
[3] *J. Soc. Chem. Ind.*, 1885, **4**, 448.
[4] *Gasanalytisches Methoden*, 4th edn., p. 181.
[5] *Zeitsch. anorg. Chem.*, 1906, **50**, 382.

concentration around 50·8 per cent. H_2SO_4, the solubility of nitric oxide is almost constant at 0·0115 c.c. per c.c. of acid, at 18° C. and 760 mm., while with 90 per cent. H_2SO_4 the solubility is 0·193 c.c. per 10 c.c. sulphuric acid, which is appreciably less than Lunge's figure. No definite solubility could be found for 98 per cent. H_2SO_4, as the mercury slowly dissolved in the acid.

The value for the solubility of nitric oxide in sulphuric acid is important, as previously stated, from the point of view of the nitrometer estimation. According to the author's experience the solubility given by Lunge is too high when sulphuric acid containing 91–92 per cent. H_2SO_4 is used in the nitrometer, the value due to Tower giving the more accurate results.

Nitric oxide is also appreciably soluble in alcohol, the absorption coefficient being 0·3161 at 0° C.[1] It is readily absorbed by aqueous solutions of certain salts, forming unstable addition compounds. Ferrous sulphate gives the compound $FeSO_4 \cdot NO$.[2] Ferrous chloride forms $FeCl_2 \cdot NO$, while copper salts give reactions and compounds of the type—

$$CuR_2 + NO \rightleftharpoons CuR_2 \cdot NO.$$

Similar compounds have also been shown to exist with the halides of iron, copper, bismuth, silicon, and boron,[3] e.g. $BiCl_3 \cdot NO$; $Fe_2Cl_6 \cdot NO$; $2Fe_2Cl_6 \cdot NO$.

Manchot[4] has also isolated a compound of the type $Fe(NO) \cdot HPO_4$.

In all these reactions an equilibrium is ultimately established of the type—

$$FeR_2 + NO \rightleftharpoons FeR_2 \cdot NO$$

and the nitric oxide is not completely absorbed, but always has an appreciable vapour pressure in contact with the solution. In consequence, the absorption of nitric oxide by any of the above solutions, as a means of estimating the volume percentage of the gas in a gaseous mixture, gives inaccurate results. This is not the case with the absorbent proposed by

[1] Carius, *Annalen*, 1885, **94**, 138.
[2] Manchot and Zechentmayer, *Annalen*, 1906, **350**, 368.
[3] Besson, *Compt. rend.*, 1889, **108**, 1012.
[4] *Ber.*, 1914, **47**, 1601.

Divers,[1] who showed that a slightly alkaline solution of sodium sulphite, Na_2SO_3, absorbs nitric oxide quantitatively, with the production of $Na{\cdot}N_2O_2SO_3$ or $Na_2SO_3{\cdot}2NO$ (sodium hyponitrososulphonate).

One part of ferrous sulphate dissolved in two parts of water will absorb three volumes of nitric oxide, while a saturated solution of ferrous chloride (slightly acidified with HCl to prevent frothing) will absorb 22 volumes. Nitric oxide is also absorbed by ortho-phosphoric acid [2] and by ortho-arsenic acid, and a number of organic acids.

It reacts with oxidizing agents, both solid and in solution. Shaken with potassium bichromate solution, or acidified permanganate, nitric oxide is oxidized to nitric acid, which oxidation is also effected by iodine solution and by hydrogen peroxide.[3] The latter may hence be used in the estimation of the gas.

When passed over heated lead dioxide, manganese dioxide, or sodium peroxide, nitric oxide forms a mixture of the corresponding nitrite and nitrate. Alkaline pyrogallol reduces nitric oxide to nitrous oxide, and this point must be borne in mind when absorbing oxygen by this reagent, in the presence of nitric oxide.[4] Chlorine peroxide oxidizes nitric oxide to nitrogen tetroxide, while hypochlorous acid yields nitric acid.

Nitric oxide is slowly decomposed by caustic potash forming potassium nitrite and gaseous nitrogen and nitrous oxide.[5] Emich [6] states that nitrous oxide is not produced in this reaction.

Moser [7] states that nitric oxide cannot be preserved indefinitely over water, owing partly to the dissolved oxygen and partly to the hydrions of the water. The following reactions probably occur :—

$$4NO + 2H_2O = 2HNO_2 + H_2N_2O_2$$
$$H_2N_2O_2 = N_2O + H_2O$$
$$3H_2N_2O_2 = 2N_2O_3 + 2NH_3$$
$$NH_3 + HNO_2 = [NH_4NO_2] = N_2 + 2H_2O$$

[1] *Chem. Soc. Trans.*, 1899, **75**, 82.
[2] Reinsch, *J. pr. Chem.*, 1843, **28**, 385.
[3] Schönbein, *J. pr. Chem.*, 1860, 265.
[4] Oppenheimer, *Ber.*, 1903, **36**, 1744.
[5] Russell and Lepraik, *Chem. Soc. Abstr.*, 1877, ii, 37.
[6] *Monatsh.*, 1892, **13**, 90.
[7] *Zeitsch. anal. Chem.*, 1911, **50**, 401.

the quantity of nitrogen increasing with the length of time the gas remains over water. Nitric oxide can, however, be kept unchanged over mercury, even in the moist condition.

Nitric oxide is reduced by a number of reducing agents. Hydrogen sulphide, sulphurous acid, alkali sulphides, and

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thesis that the oxidation of nitric oxide takes place in two stages, nitrogen trioxide first being formed, which is then further oxidized to nitrogen tetroxide.

$$(a)\ 2NO + \tfrac{1}{2}O_2 \rightleftharpoons N_2O_3.$$

$$(b)\ N_2O_3 + \tfrac{1}{2}O_2 \rightleftharpoons N_2O_4.$$

Since nitrogen trioxide is almost immediately evident on adding oxygen to nitric oxide, while nitrogen tetroxide does not appear until an appreciable time has elapsed, Raschig concluded from approximate measurements that the reaction velocities in (*a*) and (*b*) above were of the order 100 : 1. This view of the mechanism of the reaction seems also to be supported by the work of Schmidt and Böcker [1] and by that of Leblanc.[2]

On the other hand Lunge [3] contended that the primary product of the oxidation is nitrogen tetroxide. and in a further paper [4] showed that the reaction between nitric oxide and oxygen was of the third order. A somewhat lengthy controversy ensued. Both Raschig and Lunge agreed that a mixture of nitric oxide and nitrogen tetroxide is absorbed quantitatively by concentrated sulphuric acid as nitrogen trioxide, with the formation of nitrosyl sulphuric acid. With a solution of caustic soda, the absorption of the mixture was apparently only 90 per cent. theoretical, but Klinger [5] showed that the presence of water was the disturbing factor, and that by using solid potash as an absorbent, an equimolecular mixture of nitric oxide and nitrogen tetroxide was quantitatively absorbed as N_2O_3.

$$2KOH + N_2O_3 = 2KNO_2 + H_2O$$

whereas if water were present the mixture first reacted with the water thus :—

$$N_2O_3 + H_2O = 2HNO_2$$

and then part of the nitrous acid decomposed before neutralization.

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

[1] *Ber.*, 1906, **39**, 1368.
[2] *Zeitsch. Elektrochem.*, 1906, **12**, 541.
[3] *Zeitsch. angew. Chem.*, 1906, **19**, 807.
[4] Lunge and Berl, *Zeitsch. angew. Chem.*, 1907, **20**, 1717.
[5] *Zeitsch. angew. Chem.*, 1914, **27**, 7.

The possibility of existence of gaseous nitrogen trioxide which was raised by this controversy was considered by Ramsay,[1] who concluded that under ordinary conditions nitrogen trioxide is almost completely dissociated into a mixture of nitric oxide and nitrogen tetroxide. The work was repeated, however, by Dixon and Peterkin,[2] who showed that nitrogen trioxide did actually exist in equilibrium with nitric oxide and nitrogen tetroxide, according to the equation

$$N_2O_3 \rightleftharpoons NO + NO_2,$$

but that the proportion of undissociated N_2O_3 present at 760 mm. was only of the order of 3 per cent. It is probable, therefore, that the existence of the equilibrium at ordinary temperatures offers an explanation of the facts observed by both Raschig and Lunge. During the oxidation, any nitrogen tetroxide formed would be continuously removed in the presence of an absorbent, with an equivalent of nitric oxide, as N_2O_3. Bodenstein[3] has recently shown that the reaction between nitric oxide and oxygen is strictly of the third order, and furthermore that the velocity constant has a slight negative temperature coefficient. This latter fact had previously been observed by Foerster and Blich.[4]

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It is evident, therefore, that since nitrogen trioxide does exist in equilibrium with nitric oxide and nitrogen tetroxide at ordinary temperatures, the determinations of reaction velocities carried out by both Lunge and Raschig cannot be considered as giving correct information as to the order of the reaction unless more than 50 per cent. of the nitric oxide had been allowed to oxidize, and therefore Raschig's assumption that nitric oxide is oxidized rapidly to nitrogen trioxide, and then slowly to the tetroxide, cannot be accepted as correct, although Jolibois and Sanfourche[5] have recently put forward further evidence in support of Raschig's view.

Since the reaction is strictly of the third order, and if we assume that the N_2O_4 produced by the oxidation is completely dissociated (an assumption which is reasonable on

[1] *Chem. Soc. Trans.*, 1890, **57**, 590.
[2] *Chem. Soc. Trans.*, 1899, **75**, 629.
[3] *Chem. Zentr.*, 1918, ii., 333.
[4] *Zeitsch. angew. Chem.*, 1910, **22**, 2017.
[5] *Compt. rend.*, 1919, **168**, 235.

account of the relatively low vapour pressure of the tetroxide in the resulting mixture), we can represent the oxidation by the equation

$$2NO + O_2 \rightleftharpoons 2NO_2.$$

If the decrease in total volume during the reaction be ignored, therefore, the reaction velocity is expressed by the equation

$$\frac{dx}{dt} = K(a - x)^2(c - x)$$

where $2a$ = initial concentration of NO.
c = initial concentration of oxygen.

As an example of the calculation of the velocity constant (K) from these results, consider the second interval of time from 1·76 secs. to 2·64 secs.

Volume of air = 500 c.c. ($\frac{1}{5}$th = oxygen).

Volume of NO = 125 c.c.

Then $t = 2{\cdot}64 - 1{\cdot}76 = 0{\cdot}88$ secs.

$$a = \frac{47{\cdot}51}{2 \times 473{\cdot}75} = 0{\cdot}05016$$

$$c = \frac{53{\cdot}75}{473{\cdot}75} = 0{\cdot}1134$$

$$x = \frac{4{\cdot}42}{473{\cdot}75} = 0{\cdot}00933$$

$$\therefore K = \frac{1}{0{\cdot}88} \cdot \frac{1}{(0{\cdot}06324)^2} \left\{ \frac{6{\cdot}32 \times 0{\cdot}933}{5{\cdot}016 \times 4{\cdot}0827} + \log_e \left(\frac{11{\cdot}34}{5{\cdot}016} - \frac{4{\cdot}0827}{10{\cdot}407} \right) \right\}$$

$$= 47{\cdot}83.$$

Table 4 shows the values of K so calculated, and also indicates the percentage decrease in volume which has occurred for the period for which K is calculated. These results are expressed in the curve (Fig. 1), which enables values of K to be obtained by extrapolation, when the volume change is greater than that corresponding to the value of K which is being used for calculation of any one time of oxidation.

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TABLE 4

Time Interval (Seconds).	K.	Per cent. decrease in Vol. of System.
0 to 1·76	49·97	5·25
1·76 ,, 2·64	47·83	0·93
2·64 ,, 3·90	47·73	0·82
3·90 ,, 7·92	48·98	1·24
7·92 ,, 13·78	30·98	0·51
13·78 ,, 29·92	39·38	0·71

As an example of the method of calculating the time of oxidation of a given mixture of nitric oxide and air, consider

the time required to oxidize 90 per cent. of the nitric oxide in a mixture containing 25 per cent. of that gas and 75 per

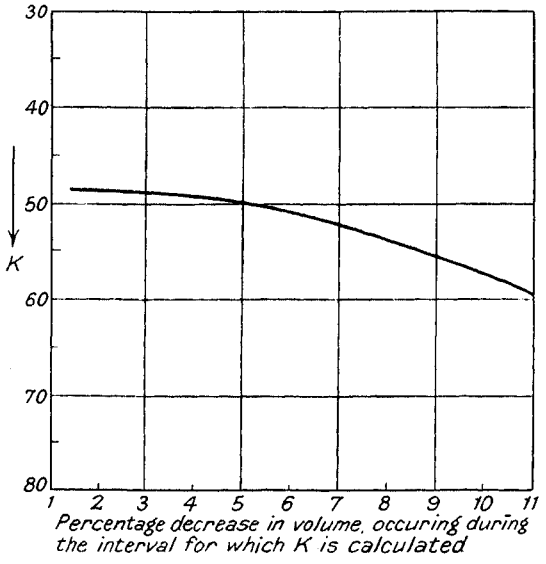

FIG. 1.

cent. of an equimolecular mixture of nitrogen and oxygen.

$$\left.\begin{aligned} NO &= 25 \\ O_2 &= \frac{75}{2} \\ N_2 &= \frac{75}{2} \end{aligned}\right\} \text{Total} = 100.$$

When 90 per cent. of the NO has been oxidized

$$a = 0{\cdot}0125$$

$$c = 0{\cdot}375$$

$$x = \frac{0{\cdot}25 \times 0{\cdot}09}{2 \times 100} = 0{\cdot}01125$$

$\therefore\ t = \dfrac{257{\cdot}6}{K}$ by substitution of the above values in the equation.

The percentage decrease in volume in this change is 11·25, and K by extrapolation from the curve would be approx. 61.

Hence $$t = \frac{257{\cdot}6}{61} \text{ secs.}$$

$$= 4{\cdot}22 \text{ secs.}$$

Taking K = 50 as a mean value, the times of oxidation

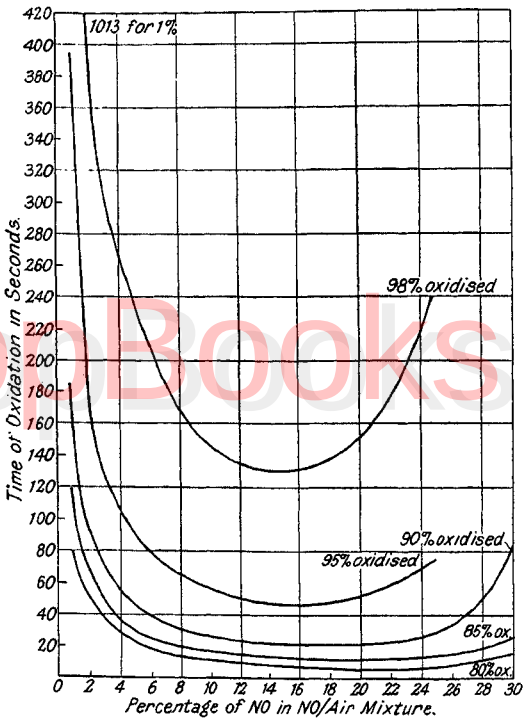

FIG. 2.

Curve showing time required to bring various mixtures of NO + Air to different stages of oxidation calculated from values given by Lunge and Berl, *Zeitsch. angew. Chem.*, 1906, **19**, 860

Times calculated from the equation

$$t = \frac{1}{50} \cdot \frac{1}{(c-a)^2} \left\{ \frac{(c-a)x}{a(a-x)} + \log_{\cdot} \frac{a(a-x)}{a(c-x)} \right\}$$

$2a$ = NO concentration (initial)
c = O_2 " "
x = change in concentration of oxygen in time t.

of various mixtures of nitric oxide and air have been calculated and the values so obtained expressed as curves (Fig. 2).

These results are sufficiently accurate to be used in practice,

but in order to obtain more accurate results use can be made of an expression for the reaction velocity due to Wegscheider [1] which takes account of the change in volume during the reaction.

Originally it was assumed that the equation

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

correctly represents the reaction. With far-reaching oxidation of the nitric oxide, however, and consequently increasing concentration of tetroxide, the change may be more accurately represented as follows :—

$$2NO + O_2 \rightleftharpoons 0{\cdot}5N_2O_4 + 0{\cdot}5(2NO_2) \quad . \quad . \quad . \quad (2)$$

which assumes that only one-half of the N_2O_4 is dissociated.

According to Wegscheider, the expression

$$\frac{d\mu}{dt} = \frac{K(M_1 - 2\mu)^2(M_2 - \mu)}{\left(V - \frac{RT}{P}b\mu\right)^2}$$

affords correct values for the reaction constant of equation (1) above when $b = 1$, and of equation (2) when $b = 1{\cdot}5$;

where M_1 = Initial volume (or number of gram-mols.) of nitric oxide.

M_2 = Initial volume (or number of gram-mols.) of oxygen.

μ = Volume of oxygen changed in time t in 100 volumes of mixture.

V = Total initial volume of gas at temperature T and pressure P, these two latter being constant under the conditions of the experiment.

On integration, the following expression for K is obtained

$$K = \frac{1}{t}\left[\frac{(2a - bc)^2}{4(2 - c)(c - 2x)} - \frac{1}{4}\left\{b^2 - \frac{4(a - b)^2}{(c - 2)^2}\right\}\log_e(c - 2x)\right.$$

$$\left. - \frac{(a - b)^2}{(c - 2)^2}\log_e(1 - x) - \frac{(2a - bc)^2}{4(2 - c)c} + \frac{1}{4}\left\{b^2 - \frac{4(a - b)^2}{(c - 2)^2}\right\}\log_e c\right]$$

where $a = \frac{100}{M_2}$; $c = \frac{M_1}{M_2}$ and $x = \frac{\mu}{M_2}$ (i.e. fraction of initial volume of oxygen which is used up in time t).

[1] *Zeitsch. physikal. Chem.*, 1900, **35**, 577.

The reaction constants can now be calculated, using Lunge's experimental values, and assuming half dissociation and complete dissociation of the N_2O_4. (See Table 5.)

TABLE 5

Reaction Time. t Seconds.	Fraction of total Oxygen used up in Time t. $= x$.	Complete Dissociation. K_1.	Half Dissociation. K_2.
1·76	0·3280	11·63	11·22
2·64	0·3833	11·71	11·20
3·96	0·4315	11·56	10·96
7·92	0·5035	11·91	11·12
13·78	0·5330	10·11	9·37
29·92	0·5736	9·92	9·07

Fig. 3 shows the times of oxidation of various mixtures of nitric oxide and air, and Fig. 4 of mixtures of nitric oxide with equal volumes of nitrogen and oxygen calculated from the corrected expression.

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The curves indicate several interesting points.

(*a*) In the case of mixtures of nitric oxide and air the most rapid oxidation occurs when the percentage of nitric oxide in the mixture is between 17–20 per cent.

(*b*) In the case of the enriched air mixtures, the minimum time of oxidation is shown with gaseous mixtures containing 30–35 per cent. of nitric oxide although these minimum values depend in each case upon the degree to which the oxidation is carried, e.g. 80 per cent. of the nitric oxide in a 20 per cent. mixture of nitric oxide and air requires a shorter time to oxidize than 80 per cent. of the nitric oxide in a 17·5 per cent. mixture, but 95 per cent. of a 17·5 per cent. mixture requires less time to oxidize than 95 per cent. of a 20 per cent. mixture.

The composition of the mixture which has the minimum time of oxidation can, of course, be calculated from the equation previously given by differentiation and equation to zero.

The work of Bodenstein [1] on the variation of the velocity

[1] *Zeitsch. Elektrochem.*, 1918, **24**, 183.

constant with temperature has also been adapted to enlarge the application of the curves to all temperatures between 0°–90° C., the curves previously given being true for temperatures at or near 30° C.

Bodenstein worked at pressures much lower than atmo-

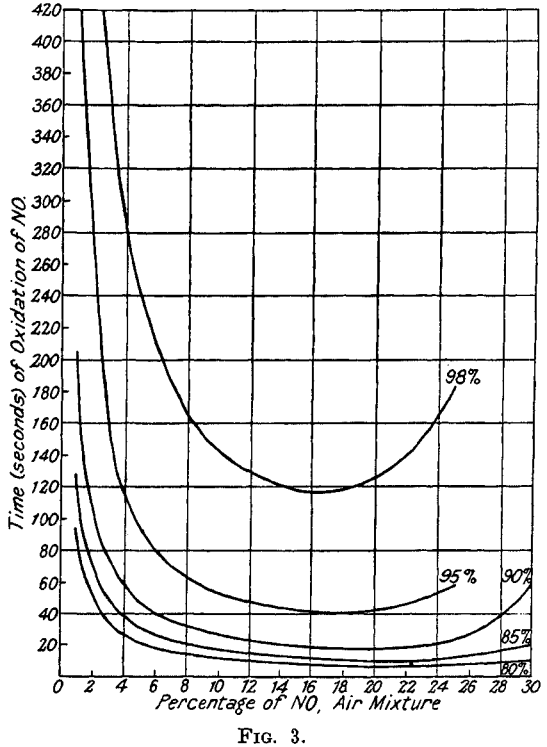

FIG. 3.

Curves showing time (seconds) required to bring various mixtures of NO and Air to different stages of oxidation, calculated on the assumption that the nitrogen tetroxide is half dissociated and therefore that

$$2NO + O_2 \rightarrow 0{\cdot}5N_2O_4 + 0{\cdot}5(2NO_2).$$

See Lunge and Berl, *Zeitsch. angew. Chem.*, 1907, 20, 1717.

spheric, and hence the concentration of N_2O_4 molecules in the equilibrium

$$2NO_2 \rightleftharpoons N_2O_4$$

was very small, and could be taken into account by applying a small correction, especially since the above equilibrium is

attained very rapidly.[1] The volume of the gas mixture during the reaction was kept constant, and the progress of the reaction followed by noting the change in pressure.

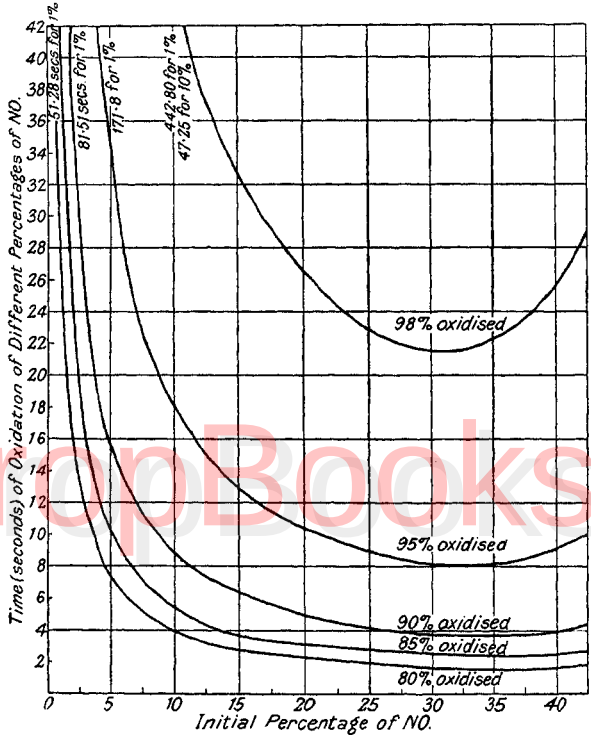

FIG. 4.

Oxidation of Nitric Oxide by a Mixture of Equal Volumes of Nitrogen and Oxygen. Curves showing the times (seconds) of oxidation of various percentages of the nitric oxide in different mixtures of that gas with a mixture of equal volumes of nitrogen and oxygen.
Times are calculated on the assumption that

$$2NO + O_2 \rightarrow 0{\cdot}5N_2O_4 + 0{\cdot}5(2NO_2)$$

represents the reaction.
See Lunge and Berl, *loc. cit.*

The concentrations of the gases in Bodenstein's paper were expressed in terms of

$$\frac{\text{Partial pressure}}{\text{Total corrected pressure}}$$

In order, therefore, to compare the constants obtained at

[1] Argo, *J. Phys. Chem.*, 1914, **18**, 438.

various temperatures by Bodenstein with those of Lunge and Berl, the concentrations in the latter experiments have been converted into pressure units in millimetres of mercury, and since also the time is expressed in minutes in the former's calculations, and in seconds in the latter's calculations, it can be shown that the constants due to Bodenstein can be expressed in the same units as the constant used in drawing up the curves (Figs. 2–4) by multiplying by the factor

$$\frac{1}{(0{\cdot}0001512)^2 \times 60} = 7{\cdot}29 \times 10^5$$

e.g. consider the curve (Fig. 5) showing the variation of the velocity constant with temperature due to Bodenstein. The value of the constant read from the curve at 20° C. is

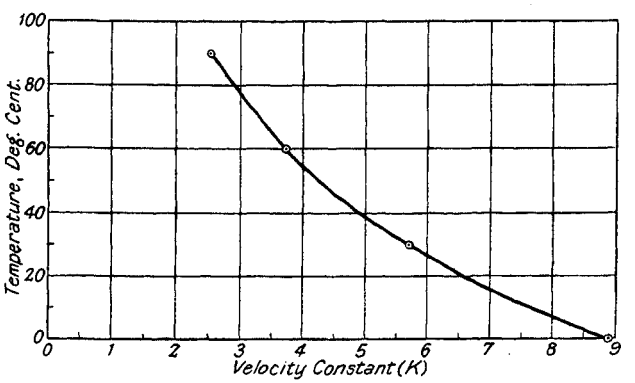

FIG. 5.—Variation of Velocity Constant (K) with Temperature.
Bodenstein, *Zeitsch. Elektrochem.*, 1918, 34, 183.

$6{\cdot}57 \times 10^{-5}$. To convert this into the units employed in Figs. 2, 3, and 4 we have

$$K = 6{\cdot}57 \times 10^{-5} \times 7{\cdot}29 \times 10^5 = 47{\cdot}91$$

which agrees with the constant calculated from Lunge and Berl's results for the same temperature (20° C.).

In order to determine the time of oxidation of any given mixture of nitric oxide and oxygen, therefore, at temperatures between 0°–90° C., it is only necessary to read off from the curve (Fig. 5) the appropriate constant for that temperature, convert it into the same units as those used in calculating the time shown in the curves (Fig. 2), and use this constant

for calculating the time of oxidation. For example, the time of oxidation at 0° C. of 98 per cent. of a 10 per cent. mixture of nitric oxide with air is required. The constant used for 20° C. was 50, and the time required at this temperature from the curve (Fig. 2) is 146·6 secs.

From the curve (Fig. 5) the velocity constant at 0° C. $= 8{\cdot}9 \times 10^{-5}$

or in the original units $= 8{\cdot}9 \times 10^{-5} \times 7{\cdot}29 \times 10^{5}$
$= 64{\cdot}9.$

Therefore the time required at 0° C. to allow the required amount of oxidation is

$$\frac{146{\cdot}6}{64{\cdot}9} \times 50 = 113 \text{ secs.}$$

The tables can thus be extended to include most gaseous temperatures liable to occur in industry, and while containing errors of a few per cent. on the longer times of oxidation, the values are on the whole approximately correct.

A more recent set of calculations on the time of oxidation of nitric oxide is due to Todd,[1] who has calculated values for the oxidation considering it as (*a*) a constant volume reaction and (*b*) a constant pressure reaction. The values obtained by him are similar to those given in the curves already shown, and for details of his method the reader is referred to his original paper.

Nitrogen Trioxide, N_2O_3 (Nitrous anhydride)

When nitric oxide and nitrogen tetroxide are mixed, or when the necessary theoretical proportion of oxygen is added to nitric oxide, a gas is obtained which behaves as if it had the composition denoted by the formula N_2O_3. It can be condensed to a deep blue liquid, and finally a solid of the same composition.

It behaves chemically in all three phases as if its composition were N_2O_3, e.g. it is completely absorbed by solid caustic potash with the formation of potassium nitrite. It is absorbed rapidly by sulphuric acid with the formation of nitrosyl sulphuric acid.[2]

[1] *Phil. Mag.*, 1918, **35**, 281.
[2] Lunge and Berl, *Zeitsch. angew. Chem.*, 1907, **20**, 1717.

In its physical properties, however, nitrogen trioxide behaves as if it were an equimolecular mixture of nitric oxide and nitrogen tetroxide.

Preparation. 1. Nitrogen trioxide may readily be prepared by the reduction of nitric acid with arsenious oxide, starch, cane sugar, and a number of similar substances. By using ordinary concentrated nitric acid of sp. gr. = 1·5, a very large proportion of nitrogen tetroxide is simultaneously evolved. According to Lunge,[1] practically pure nitrogen trioxide is obtained by the action of arsenious acid on nitric acid of sp. gr. = 1·35, but for most experimental purposes the trioxide prepared in this way will be found to contain too large a proportion of nitrogen tetroxide as impurity. Ramsay and Cundall [2] recommend the use of a nitric acid of sp. gr. = 1·5. The fundamental reaction taking place is then as follows [3]:—

$$As_4O_6 + 4HNO_3 = 4HAsO_3 + 2N_2O_3.$$

The arsenious oxide and nitric acid, in the proportions required by the above equation, are carefully heated on a water-bath in a large retort or flask until the reaction begins, when the source of heat is immediately removed. As the reaction is liable to become violent, a dish of cold water should be at hand to moderate the reaction in its initial stages. The gas is dried by passing it over fused calcium nitrate, and then over phosphorus pentoxide to remove nitric acid vapour, and is finally cooled in U tubes surrounded by an ice-salt freezing mixture. A blue or bluish-green liquid is thus obtained, the blue-green colour invariably predominating if nitrogen tetroxide is present in quantity. The liquid is then distilled in a current of nitric oxide, and the vapours passed over anhydrous calcium nitrate or phosphorus pentoxide and reliquefied.

In this way a deep blue, mobile liquid is obtained, of the composition corresponding to the formula N_2O_3. It is very difficult to remove the last trace of tetroxide from the trioxide.

2. Nitrogen trioxide may also be prepared by adding to nitric oxide the theoretical quantity of oxygen to form N_2O_3.

$$4NO + O_2 \rightleftharpoons 2N_2O_3.$$

[1] *Ber.*, 1878, **11**, 1229. [2] *Chem. Soc. Trans.*, 1885, **47**, 187.
[3] Ramsay, *ibid*, 1890, **58**, 590.

The trioxide is then liquefied by immersing the tube containing the gases in a freezing mixture.

At temperatures below $-100°$ C., the final product of oxidation of a mixture of nitric oxide and oxygen in any proportion is nitrogen trioxide.[1]

3. Nitrogen trioxide is also formed when a spark discharge is allowed to pass through liquid air.[2]

The trioxide first appears as a flocculent green precipitate in the liquid air, and after evaporation of the latter a light blue amorphous powder is obtained, which assumes a permanent blue colour on melting and resolidification. Helbig states that with a potential difference of 1,000 volts the yield was approximately 0·5 gm. trioxide per 100 c.c. liquid air.

4. When mineral acids act upon a nitrite, nitrogen trioxide is produced, owing to the production and decomposition of nitrous acid, which is very unstable, and which in concentrated solution decomposes into nitrogen trioxide.

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O.$$

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5. Nitrogen trioxide is obtained by treatment of nitrosyl sulphuric acid (chamber crystals) with water.

$$SO_2\!<\!\begin{matrix}OH\\ONO\end{matrix} + H_2O \rightarrow SO_2\!<\!\begin{matrix}OH\\OH\end{matrix} + [HNO_2].$$

The nitrous acid then splits up as in method (4).

6. Nitrogen trioxide may also be obtained by treating nitrogen tetroxide with a small quantity of water,

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2,$$

the nitrous acid splitting up as before.

7. Nitrogen trioxide is quantitatively produced by reduction of nitrogen tetroxide with nitric oxide.[3]

$$N_2O_4 + 2NO \rightleftharpoons 2N_2O_3.$$

The reaction is best carried out by saturating liquid nitrogen tetroxide with gaseous nitric oxide and on subsequent cooling

[1] Francesconi and Sciacca, *Gazzetta*, 1904, **34**, 1447.

[2] Helbig, *Atti R. Accad. Lincei*, 1903, [V.], **12**, i. 166; Müller, *Zeitsch. anorg. Chem.*, 1912, **72**, 330; Raschig, *ibid*, 1913, **84**, 115.

[3] Péligot, *Ann. Chim. Phys.*, 1841, [iii.], **2**, 58; Porschnew, *Zeitsch. anorg. Chem.*, 1894, **7**, 214.

dark blue crystals of the trioxide separate. Wittorf[1] has shown that no other compound is formed in the reaction and that the eutectic mixture contains 63·6 per cent. NO_2 and 36·4 per cent. NO and melts at $-112°$.

Properties. Liquid nitrogen trioxide has no very definite boiling-point, the approximate temperature being $-2°$ C. It solidifies at $-111°$[2]; $-103°$.[3] The sp. gr. of the liquid at 0° C. is 1·449.[4] When quite dry it does not boil until 43° C.[5]

At ordinary temperatures nitrogen trioxide has a vapour density which is in accord with the possibility that the gas consists of an equimolecular mixture of NO and NO_2.[6] Ramsay showed that practically no change in volume occurred on adding nitric oxide to nitrogen tetroxide in equivalent quantity, but Dixon and Peterkin[7] pointed out that the volume should, in fact, have increased, owing to the dissociation of the N_2O_4 molecules on dilution, and were able to show, therefore, that approximately 3 per cent. of undissociated N_2O_3 molecules were present.

Baker[8] adduced further evidence in support of the existence of gaseous N_2O_3, by showing that when quite dry the vapour density of the gas was in accord with the formula N_2O_3.

There has been a lengthy controversy as to whether nitrogen trioxide is the first product of oxidation of nitric oxide by oxygen (see under nitric oxide), but it is now generally accepted that nitrogen tetroxide is the primary product, and that the nitrogen trioxide is produced as a result of the secondary equilibrium set up between the nitrogen tetroxide and unoxidized nitric oxide. Several observers, in particular Foerster and Blich,[9] have shown that the trioxide is more rapidly absorbed by alkalies and by concentrated sulphuric acid than is the tetroxide, but on the other hand is more slowly absorbed by water. Liquid nitrogen trioxide at $-22°$ C., for example, is immediately absorbed by caustic soda solution, whereas liquid nitrogen tetroxide is only attacked very slowly.

[1] *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 857.
[2] Helbig. [3] Wittorf.
[4] Geuther, *Annalen*, **245**, 97.
[5] Baker, *Chem. Soc. Trans.*, 1912, **101**, 2339.
[6] Ramsay and Cundall, *Chem. Soc. Trans.*, 1890, **57**, 590.
[7] *Chem. Soc. Trans.*, 1899, **75**, 614.
[8] *Chem. Soc. Trans.*, 1907, **91**, 1862.
[9] *Zeitsch. angew. Chem.*, 1910, **22**, 2017.

On absorption in concentrated sulphuric acid, nitrogen trioxide yields nitrosyl sulphuric acid.

$$2SO_2{<}^{OH}_{OH} + N_2O_3 \rightleftharpoons 2SO_2{<}^{OH}_{ONO} + H_2O.$$

A similar compound with perchloric acid also exists and is obtained by passing the trioxide into concentrated perchloric acid.[1] The latter substance is obtained as light yellow leaflets and has the composition $NO{\cdot}OClO_3{\cdot}H_2O$.

Absorption of nitrogen trioxide by alkalies gives exclusively a nitrite, provided that no moisture is present.[2]

$$2NaOH + N_2O_3 = 2NaNO_2 + H_2O.$$

If water is present some formation of nitrate takes place owing to the decomposition of part of the nitrous acid produced at the moment of solution. A somewhat similar reaction takes place with water. At 0° C., and in the presence of a large excess of water, nitrogen trioxide dissolves without the evolution of any oxides of nitrogen, but in concentrated solution nitric oxide is evolved, and a bluish-green liquid containing nitrous and nitric acids is obtained.[3]

According to Lunge [4] nitrogen trioxide is reduced by sulphur dioxide in the absence of air or oxygen, even in the cold, with the production of nitrous oxide and nitrogen. If, however,

oxidation of gaseous ammonia, being formed in each case by the oxidation of the nitric oxide primarily produced.

(1) $N_2 + O_2 = 2NO$.
(2) $4NH_3 + 5O_2 = 4NO + 6H_2O$.

It is also a by-product in most nitration processes where " mixed acids " are used, e.g. in the dyestuff industry, in the production of nitro-explosives, in the manufacture of artificial silk and in processes for the denitration of waste acids.

Preparation. 1. Nitrogen tetroxide can be prepared, as already stated (see nitric oxide), by the oxidation of nitric oxide by air or oxygen.

If a mixture of nitric oxide and oxygen in the proportion of 2 : 1 by volume is dried and well mixed by passing through a tube filled with broken glass or porcelain, and then passed into a U tube immersed in a freezing mixture at $-20°$ C., a colourless crystalline mass of the tetroxide is obtained.[1]

The reaction between nitric oxide and oxygen takes an appreciable time for completion, otherwise the method is convenient for preparing small quantities of the liquid or solid material.

2. Nitrogen tetroxide is also produced when nitrates of many of the heavy metals are heated, e.g.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

The nitrates of the alkali metals do not behave in this way unless electrolysed in the fused condition.

This method of preparation is of little use where any quantity of the tetroxide is required, since relatively large quantities of lead nitrate are needed, and, in addition, the oxygen simultaneously evolved, by diluting the tetroxide, renders condensation very difficult, and a poor yield is obtained.

3. A very good method of preparation is that described by Cundall.[2] The method is based upon the fact that arsenious oxide is oxidized by concentrated nitric acid, to arsenic pentoxide, probably according to the fundamental equation[3]

$$As_4O_6 + 4HNO_3 = 4HAsO_3 + 2N_2O_3.$$

[1] Dulong, *Ann. Chim. Phys.*, 1816, [ii.], **2**, 317.
[2] *Chem. Soc. Trans.*, 1891, **59**, 1076.
[3] Ramsay, *Chem. Soc. Trans.*, 1890, **58**, 590.

If, however, concentrated sulphuric acid be present the change is probably represented by the reaction[1]

$$4HNO_3 + As_4O_6 + nH_2SO_4 = 4N_2O_4 + 2As_2O_5 \cdot 4H_2O]nH_2SO_4$$

In Cundall's method 315 grams of fuming nitric acid are mixed with 150 grams of concentrated sulphuric acid, and the cooled mixture poured on to 250 grams of coarsely powdered arsenious oxide contained in a flask of 1 litre capacity. The reaction starts at a little above air temperature, and requires external cooling by water as it is apt to become very vigorous.

It is advisable to give the evolved gases a preliminary cooling in a reflux condenser. The gas is then passed through a U tube containing phosphorus pentoxide, and finally into a pair of U tubes immersed in a freezing mixture of ice and salt. The gas attacks rubber and cork vigorously, and all-glass joints should be used, while corks should be either of asbestos or well paraffined. The distillation is stopped when the liquid in the flask begins to turn green. The liquid tetroxide obtained is liable to contain as impurities both nitric acid and nitrogen trioxide. These may be removed by treating the liquid with a mixture of fuming nitric acid and excess of phosphorus pentoxide:

$$2HNO_3 + H_2O + N_2O_5$$
$$N_2O_3 + N_2O_5 = 2N_2O_4.$$

The mixture is finally redistilled and the gas led through a tube containing powdered arsenious oxide and then reliquefied.

4. As an alternative method of preparation, the trioxide may be prepared in a similar way by treating arsenious oxide with fuming nitric acid alone. The liquid trioxide is then oxidized by gaseous oxygen. This method is slow and very wasteful, however, the evaporation produced by the stream of oxygen being very considerable.

The modification suggested originally by Ramsay (*loc. cit.*) of mixing together the arsenious oxide and sulphuric acid, and then adding the fuming nitric acid slowly to this mixture, is also unsatisfactory, owing to the interaction between the tetroxide and sulphuric acid to form nitrosyl sulphuric acid, a poor yield being obtained.

[1] Ramsay and Cundall, *Ibid.*, 1885, **53**, 187.

DropBooks

5. The tetroxide may also be prepared by the fractional distillation of fuming nitric acid. The product contains small quantities of the trioxide and of nitric acid, but the method is a useful one when fuming nitric acid is available in quantity.

6. A method of preparation due to Winans [1] consists in treating with fuming sulphuric acid a homogeneous mixture of sodium nitrate and nitrite. The homogeneous mixture of the two salts is made either by fusing them together, or alternatively by pouring a molten mixture of the salts into carbon tetrachloride. Sufficient sodium bisulphate (from a previous preparation) is added to fix the free sulphur trioxide present.

$$NaNO_3 + NaNO_2 + H_2S_2O_7 = 2NaHSO_4 + ?NO_2$$
$$2NaHSO_4 + SO_3 = Na_2S_2O_7 + H_2SO_4$$

In spite of its apparent simplicity the method gives a poor yield.

7. Nitrogen tetroxide is also evolved when Chamber crystals (nitrosyl sulphuric acid) are warmed with potassium nitrate.

$$SO_2\begin{matrix}OH\\<\\ONO\end{matrix} + KNO_3 = KHSO_4 + N_2O_4.$$

8. The tetroxide is also obtained by treatment of a nitrite, or nitrous acid, with nitric acid [2]—

$$HNO_3 + R{\cdot}NO_2 = R{\cdot}OH + N_2O_4;$$

by the electrolysis of fused alkali nitrites; and by treatment of silver nitrite with iodine—

$$2AgNO_2 + I_2 = 2AgI + N_2O_4.$$

It is also stated that a good yield of the tetroxide may be obtained by passing a mixture of air and steam through a thin-walled porcelain tube at 1,600°, the rate of diffusion of the hydrogen produced being accelerated by raising the pressure inside the tube and lowering the pressure outside the tube.[3]

Properties. Liquid nitrogen tetroxide at 15° C. is a light orange-coloured liquid, which solidifies to colourless crystals at − 10·1° C. and boils at 22° C.[4]

The general physical constants of the liquid are as follows :—

[1] D.R.P. 193,696, 1908.
[2] Girard, *Bull. Soc. Chim.*, 1878, [ii.], **30**, 531.
[3] D.R.P. 182,297, 1908.
[4] Oddo, *Chem. Soc. Abstr.*, 1915, **108**, ii., 556.

Specific gravity [1]:—

− 5° C.	= 1·5035.
0°	= 1·4935.
10°	= 1·4770.
15°	= 1·4740.
21·6°	= 1·4396.

Specific heat [2] = 0·477.

Heat of formation of (liquid) = − 2,200 cal. (for NO_2 = 46 grams).

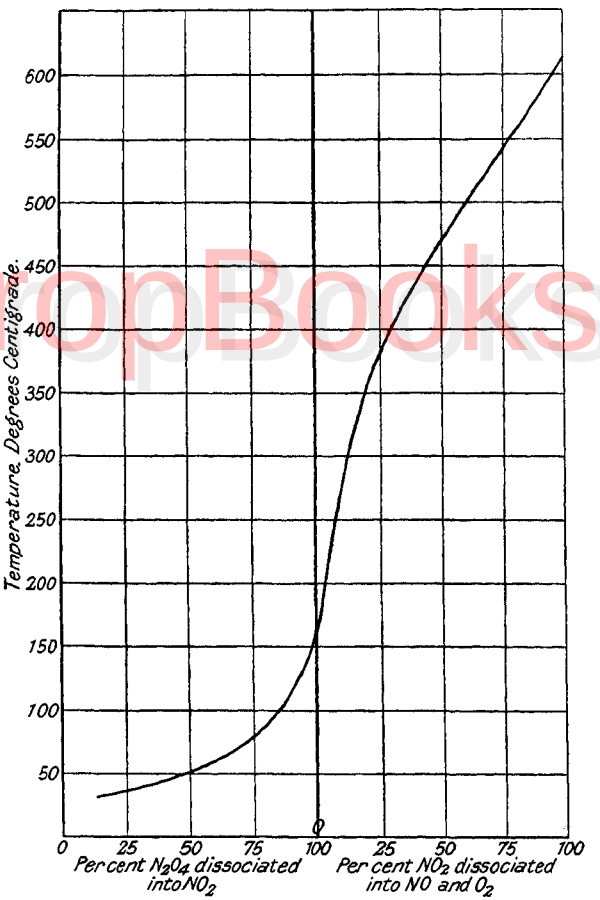

FIG. 6.—Thermal Dissociation of N_2O_4 and NO_2.
Richardson, *Chem. Soc. Trans.*, 1887, **51**, 402.

[1] Geuther, *Annalen*, 1888, **245**, 96.
[2] Ramsay, *Zeitsch. physikal. Chem.*, 1890, **5**, 221.

Heated above its boiling-point the liquid tetroxide rapidly vaporizes to an orange-brown gas of peculiar odour. At higher temperature the colour deepens, again becoming lighter, and at still higher temperatures becoming finally colourless. The colour changes are probably due to the dissociation of the N_2O_4 molecule. The tetroxide is capable of existence as pure NO_2 only between very narrow limits of temperature. At air temperatures N_2O_4 is the preponderating molecule, while at 64° C. one half of the N_2O_4 molecules have been dissociated into the simpler NO_2 molecules. Above 150° C. decomposition into nitric oxide and oxygen commences; at 184° C. 5 per cent. is dissociated; at 494° C. 56·5 per cent., and the reaction is complete at 620° C.[1]

The results of Richardson's work are shown graphically in Fig. 6.

The results show that about 15 per cent. of the N_2O_4 molecules are dissociated at ordinary temperatures.

Schreber[2] gives the following values of the dissociation constants of the reaction

$$N_2O_4 \rightleftharpoons 2NO_2.$$

$$K = \frac{(N_2O_4)^{\frac{1}{2}}}{NO_2}$$

TABLE 6

Temp. ° C.	K.
0·0	8·060
18·3	3·710
49·9	1·116
73·6	0·544
99·8	0·273

[1] Richardson, *Chem. Soc. Trans.*, 1887, **51**, 397. For other references to the dissociation of nitrogen tetroxide, see Playfair and Wanklyn, *ibid.*, 1862, **15**, 156; Deville and Troost, *Compt. rend.*, **64**, 237; Naumann, *Ber.*, 1878, **11**, 2045; Natanson, *Ann. Phys. Chem.*, 1886, **27**, 606.

[2] *Zeitsch. physikal. Chem.*, 1897, **24**, 651.

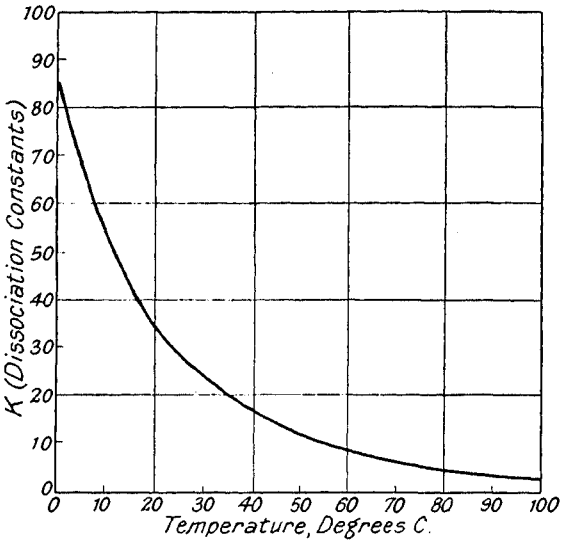

FIG. 7.—Dissociation Constants of Nitrogen Tetroxide.

$K = \frac{(N_2O_4)^1}{(NO_2)}$ Schreber, *Zeitsch. physikal. Chem.*, 1897, **24**, 651.

DropBooks

Heat of formation (Thomsen):—

$$2N + 4O = N_2O_4 - 3{,}900 \text{ (cal.)}$$

$$\begin{pmatrix} 9\%\ NO_2 \\ 91\%\ N_2O_4 \end{pmatrix}$$

Heat of dissociation:—

$$N_2O_4 \rightleftharpoons 2NO_2 - 13{,}000 \text{ cal. (approx.)}.$$

Calculated heat of formation of undissociated

$$N_2O_4 = -2{,}650 \text{ cals.}$$
$$NO_2 = -8{,}125 \text{ cals.}$$

Nitrogen tetroxide is decomposed by freely burning carbon, sulphur, and phosphorus, and is also reduced by sulphuretted hydrogen, with the production of nitric oxide.

Both potassium and sodium decompose the gas at ordinary temperatures, while many metals and lower oxides are oxidized by heating in the gas at temperatures up to 500° C.

Finely divided copper absorbs both gaseous and liquid nitrogen tetroxide at ordinary temperature, forming a maroon-coloured additive compound of the constitution Cu_2NO_2. This substance reacts violently with water, giving pure nitric

oxide and a solution containing cupric and cuprous nitrates and metallic copper. Similar compounds (nitro-metals) are obtained with cobalt and nickel.[1]

Many oxides and also metals give nitrates and nitrites on prolonged contact with the tetroxide. If the temperature of absorption is sufficiently high only nitrates are formed.

Schloesing [2] states that calcium nitrate is exclusively produced by the absorption of nitrogen tetroxide in lime at 300°–400° C. Barium oxide differs from most metallic oxides in giving a mixture of nitrite and nitrate at 200° C.[3] Many metallic salts, both in the solid state and in solution, form nitrates in contact with nitrogen tetroxide, e.g. the phosphates of magnesium, aluminium, and iron. Similar results are also obtained with silicates, borates, molybdates, tungstates, etc.

Nitrogen tetroxide exhibits a similar behaviour to nitric oxide in forming additive compounds with many metallic salts, for example, compounds such as [4]:—

$$BiCl_3 \cdot NO_2; \quad SnCl_4 \cdot NO_2; \quad FeCl_3 \cdot NO_2; \quad 4FeCl_2 \cdot NO_2; \quad 4FeBr_2 \cdot NO_2, \text{ etc.}$$

Nitrogen tetroxide dissolves readily in water with the formation of a mixture of nitric and nitrous acids.

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2.$$

The reaction can, perhaps, be most clearly represented in the following way.

$$\begin{array}{ccc} O_2N & OH & O_2N - OH \\ | & | & \rightleftharpoons \quad + \\ O_2N & H & ON - OH \end{array}$$

The nitrous acid subsequently decomposes in one of two ways. If the amount of water is relatively small, the reaction takes place approximately according to the equation

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O.$$

If an excess of water be present, however, the reaction is more nearly represented by the equation

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

[1] Sabatier and Senderens, *Compt. rend.*, 1892, **115**, 236.
[2] Eng. Pat. 22,119, 1913. [3] Dulong, *Annalen*, 1862, **122**, 18.
[4] Thomas, *Ann. Chim. Phys.*, 1898, [vii.], **13**, 145.

This latter equilibrium has been investigated by Saposchnikoff and others [1] (*vide* nitrous acid).

It is not possible to produce pure nitric acid by shaking nitrogen tetroxide with water—after a certain concentration of nitric acid is reached, the tetroxide merely dissolves, giving yellow-coloured solutions, or in the absence of air bluish-green solutions. The yellow solution obtained also contains, under favourable conditions, a small quantity (about 0·2 per cent.) of nitrous acid. The dissolved tetroxide increases the specific gravity of the nitric acid so produced.

When nitrogen tetroxide is led into water, nitric acids containing 60–65 per cent. HNO_3 can readily be obtained.[2]

It was shown by Foerster and Koch [3] that nitric acid containing 68·4 per cent. HNO_3 can be realized experimentally under these conditions, and is the maximum concentration obtainable in this way.

When liquid nitrogen tetroxide is added to a small quantity of water a separation into two layers occurs. The upper layer consists of nitric acid containing dissolved nitrogen tetroxide, while the lower bluish-green layer consists mainly of nitrogen trioxide

$$2N_2O_4 + H_2O \rightleftharpoons N_2O_3 + 2HNO_3.$$

If, however, oxygen is bubbled through the mixture, the latter assumes an orange-yellow colour and the upper layer is found to contain nitric acid of 95–99 per cent. HNO_3—while the lower layer contains nitrogen tetroxide with 5–10 per cent. HNO_3.[4]

Nitrogen tetroxide is absorbed readily by concentrated sulphuric acid, with the formation of nitrosyl sulphuric acid (Chamber crystals).

$$N_2O_4 + SO_2\langle^{OH}_{OH} \rightleftharpoons SO_2\langle^{OH}_{ONO} + HNO_3$$

It has been shown by Lunge and Weintraub [5] that this reaction is reversible, a rise in temperature causing the reaction

[1] *Chem. Zentr.*, 1900, [ii.], 708; 1901, [ii.], 330.
[2] Lunge and Berl, *Chem. Zeit.*, 1904, **28**, 1243.
[3] *Zeitsch. angew. Chem.*, 1908, **21**, ii., 2161, 2209.
[4] Eng. Pat. 319, 1911; Eng. Pat. 1,180,061, 1916.
[5] *Zeitsch. angew. Chem.*, 1899, **12**, 417.

to move from right to left. It is also evident, since nitrosyl sulphuric acid is decomposed by water, that the rate of absorption of the tetroxide by sulphuric acid will decrease, with decreasing concentration of sulphuric acid, and furthermore the nitric acid retained in the solution will reach a minimum value, which will be at a concentration of sulphuric acid in which there is sufficient free water to decompose nitrosyl sulphuric acid in the cold. This occurs with approximately 65 per cent. H_2SO_4. Caustic alkalies absorb nitrogen tetroxide quite readily, but not so rapidly as the trioxide. It should be borne in mind that the absorption of nitrogen tetroxide by aqueous alkalies consists firstly in the solution of the gas in the water present, and then in the neutralization of the nitric and nitrous acids, so produced, by the caustic soda or potash.

Since nitrous acid very quickly decomposes into nitric acid and nitric oxide, it is almost impossible to obtain the theoretical ratio of nitrate/nitrite by absorption in such aqueous solutions, and consequently the method of determining the amount of nitrogen tetroxide present in a mixture with nitrogen trioxide, by absorption in aqueous alkali, and determination of the ratio of nitrate to nitrite, gives inaccurate results. It should also be pointed out that since solution and decomposition of the nitrogen tetroxide must take place before neutralization of the resulting acids can be effected, it is useless to employ too concentrated solutions of caustic soda or caustic potash for this purpose. It can be shown that the rate of absorption of the gas in caustic soda solution increases with the concentration of caustic soda, reaching a maximum with solutions about 1·5N. With a 4N solution the rate of absorption is only equivalent to that of pure water, and higher concentrations are even less effective.

By absorption in such solutions an aqueous solution containing a nitrate and nitrite is obtained. For many commercial purposes, either salt in a state of purity is more valuable than a mixture of the two. If the passage of nitrogen tetroxide into such an absorbing solution is continued after the free alkali is neutralized, a secondary action sets in between the nitric acid produced by the tetroxide and water, and the nitrite already present, resulting in the formation of an equiva-

lent quantity of nitrate and the evolution of nitric oxide

$$NaNO_2 + HNO_3 = NaNO_3 + [HNO_2]$$

It is thus possible to produce a commercially pure nitrate by leading nitrogen tetroxide into an aqueous solution of an alkaline hydroxide, and this reaction is utilized commercially. Aqueous solutions of sodium and potassium carbonates also absorb nitrogen tetroxide, again with the production of nitrate and nitrite, and the liberation of carbon dioxide. The rate of absorption, however, is less than with caustic soda or caustic potash.

Nitrogen tetroxide is not acted upon by gaseous oxygen, but is oxidized by ozone to nitrogen pentoxide, N_2O_5. With sulphur dioxide and sulphur trioxide, nitrogen tetroxide gives a series of compounds, the constitution of which is uncertain.

Michaelis [1] states that the compound $O(SO_2 - ONO)_2$, which can be regarded as the anhydride of nitrosyl sulphuric acid, is the main product obtained by the action of sulphur dioxide on liquid nitrogen tetroxide.[2]

DropBooks

Nitrogen Pentoxide, N_2O_5 (Nitric anhydride).

Preparation. 1. Nitrogen pentoxide was discovered by Deville [3] in examining the action of dry chlorine on silver nitrate. The reaction is not evident until the nitrate has been warmed to 90°–95° C., by surrounding the U-tube containing the silver nitrate with hot water. Once the reaction has started the temperature of the water jacket can be lowered to 50°–60° C.

$$4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2.$$

2. A more convenient method of preparation, due to Meyer,[4] is by dehydration of pure nitric acid with phosphorus pentoxide. The nitric acid is first distilled two or three times with concentrated sulphuric acid; any dissolved oxides of nitrogen are removed by bubbling a slow stream of oxygen through the liquid. Phosphorus pentoxide is then added gradually

[1] *Ber.*, 1874, **7**, 1075.
[2] See also Hasenbach, *J. pr. Chem.*, 1871, ii., **4**, 4; Friedburg, *Chem. News*, 1883, **47**, 52.
[3] *Ann. Chim. Phys.*, 1849, [iii.], **28**, 241.
[4] *Ber.*, 1889, **22**, 23.

in calculated quantity and with constant cooling of the mixture. The syrupy liquid produced is poured into a dry retort, and distilled into a receiver surrounded by a freezing mixture. (A carbon filament lamp is a very useful form of heating apparatus.) An oily distillate, orange-red in colour, is obtained, which separates into two layers on standing. The upper layer is separated, and cooled to 0° C., when colourless needle-shaped crystals are deposited. These crystals are drained, melted, recrystallized, and again drained from the mother liquor.

Since the pentoxide reacts vigorously with most organic substances such as cork and caoutchouc, all apparatus must preferably be constructed to avoid the use of these substances either by fusing, or the use of ground-glass joints, or alternatively by the use of a sleeve joint constructed of tubes of different diameters, plugged with asbestos string soaked in paraffin wax. These joints are very useful in experimental work with nitrous gases, and can be made quite gastight with a little practice.

$$2HNO_3 - H_2O = N_2O_5.$$

3. Nitrogen pentoxide may also be obtained by the action of ozone on nitrogen trioxide, or on nitrogen tetroxide either in the liquid or gaseous condition.[1]

The ozone does not act catalytically in this method of preparation, only one-third of the ozone molecule having any oxidizing effect.

4. Oxidation of nitrogen to nitrogen pentoxide also takes place in the silent discharge, in the presence of ozone, which may be produced by the discharge, or also admixed separately with the nitrogen-oxygen mixture before submitting to the discharge.[2] A silent discharge may act on nitrogen-oxygen mixtures in two ways:—

(*a*) Producing a mixture of ozone and nitrogen oxides.

(*b*) Producing only nitrogen oxides. Mixtures of ozone and nitrogen oxides are produced when the gas is drawn com-

[1] Helbig, *Atti R. Accad. Lincei*, 1903, **12**, [i.], 211; *Zeitsch. Elektrochem.*, 1906, **12**, 550.

[2] Russ and Ehrlich, *Zeitsch. Elektrochem.*, 1914, **20**, 45; D.R.P. 266,345, 1912.

paratively quickly through the discharge tube, in which case the volume ratio $\frac{N_2O_5}{O_3} = 0{\cdot}019$.

To avoid the production of ozone, the gas mixture is first exposed to a spark discharge, i.e. it is charged with oxides of nitrogen and then led in a slow stream through the silent discharge tube. If the nitrogen-oxygen mixture is exposed to the silent discharge until all the accompanying ozone is used up, far-reaching oxidation to nitrogen pentoxide occurs. Russ and Ehrlich found that air to which no oxygen had been added gave 90–100 mg. of nitrogen pentoxide per litre under such treatment, while a mixture containing equal volumes of oxygen and nitrogen yielded, under similar conditions, about 250 mg. of nitrogen pentoxide. In an actual experiment, using a Siemens' tube with a distance of 4 mm. between the electrodes, and a discharge space of 140 c.c., a concentration of 200 mg. of the pentoxide per litre was obtained, with a 50-periodicity A.C. current at 15,000 volts. The gas-mixture contained equal volumes of oxygen and nitrogen and was led through the tube at the rate of 4 c.c. per minute.

5. Nitrogen pentoxide may be obtained in a single operation by the fractional distillation of a mixture of nitric acid and phosphorus pentoxide, in a current of ozonized oxygen, which prevents decomposition of the pentoxide into oxygen and the lower oxides of nitrogen. The pentoxide can be almost completely condensed at $-8°$ C.

The vapour pressure of the pentoxide reaches about one atmosphere at 34° C. It is possible to oxidize nitrogen tetroxide dissolved in nitric acid, electrolytically, and solutions of nitric acid containing up to 20 per cent. of nitrogen pentoxide can be obtained in this way.

Properties. Nitrogen pentoxide crystallizes in colourless rhombic plates of sp. gr. 1·63. It melts with slight decomposition at 29·5° C. At its melting-point, nitrogen pentoxide develops a strong yellow colour, and on further heating vigorous decomposition occurs, with copious evolution of nitrogen tetroxide mixed with oxygen.

$$2N_2O_5 = 2N_2O_4 + O_2.$$

The reaction is explosively violent, if the substance is

rapidly heated, and care must be exercised in its preparation.

Thermochemical data :

$$N_2 + 5O = N_2O_5 \text{ (gas)} + 1{,}200 \text{ cal.}$$
$$N_2 + 5O = N_2O_5 \text{ (liq.)} + 3{,}600 \text{ cal.}$$
$$N_2 + 5O = N_2O_5 \text{ (solid)} + 11{,}800 \text{ cal.}$$
$$N_2 + 5O = N_2O_5 \text{ (dissolved)} + 28{,}600 \text{ cal.}$$

Heat of solution [1] = 16,800 cal.

Owing to the ease with which the pentoxide loses an atom of oxygen, it is a powerful oxidizing agent, and like nitrous oxide vigorously supports the combustion of burning carbon, sulphur, phosphorus, etc. Nitrogen pentoxide is also a useful nitrating agent, and the method of preparation in quantity for this purpose is described by Gibson.[2]

In general the action of the pentoxide with organic substances proceeds to the same stage of nitration as if a mixture of nitric and sulphuric acids were used.

Nitrogen pentoxide is also soluble in nitric acid—a behaviour analogous to that of sulphur trioxide and sulphuric acid. A definite compound, $N_2O_5 \cdot 2HNO_3$, which is a liquid at ordinary temperatures, has been isolated. When dissolved in carbon tetrachloride solution, together with sulphur trioxide, a crystalline precipitate (m.p. 124°-128°) is obtained of the probable composition [3]

$$O\begin{matrix} \nearrow SO_2 \cdot O \cdot SO_2 \cdot O \cdot NO_2 \\ \searrow SO_2 \cdot O \cdot SO_2 \cdot O \cdot NO_2 \end{matrix}$$

Schultze [4] describes a somewhat similar compound which is obtained by leading gaseous sulphur trioxide into concentrated nitric acid or into a mixture of concentrated nitric acid with sulphuric acid. On cooling a colourless crystalline product (m.p. 93°–104° C.) is obtained of the composition $N_2O_5(SO_3)H_2O$.

[1] Thomsen, *Ber.*, 1879, **12**, 2062.
[2] *Proc. Roy. Soc. Edin.*, 1908, **28**, 705.
[3] Pictet and Karl, *Compt. rend.*, 1907, **145**, 238.
[4] U.S.P. 1,047,576, 1913; *J. Soc. Chem. Ind.*, 1913, 84.

The Oxyacids of Nitrogen

Nitrous Acid, HNO_2

Nitrous acid is formed in most reactions where nitric acid acts as an oxidizing agent, and in some cases as a nitrating agent, but is difficult to isolate from such reaction mixtures.

Preparation. 1. It may be obtained in very dilute solution by leading nitrogen trioxide, or an equimolecular mixture of nitric oxide and nitrogen tetroxide, into ice-cold water.

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2.$$

2. An aqueous solution may also be prepared by the action of dilute hydrochloric acid on aqueous silver nitrite.

$$AgNO_2 + HCl = AgCl + HNO_2.$$

3. Mixed with inorganic salts, solutions of nitrous acid are readily obtained by treating alkali nitrites with dilute acids. Since the alkali nitrites are easily prepared, this method of preparation is usually the most convenient for laboratory purposes. Sodium or potassium nitrite may be obtained quite readily in a state of purity by passing nitrogen trioxide, or a mixture of nitric oxide and tetroxide, containing an excess of nitric oxide, into an aqueous solution of sodium or potassium hydroxide.[1] The nitrous gases from the arc process and from the catalytic oxidation of gaseous ammonia have also been adapted for the manufacture of sodium nitrite, by allowing them to oxidize only so far as N_2O_3 and then absorbing them in caustic alkalis with the production of almost pure nitrites.

Many nitrates are also reduced to nitrites by fusion with lead, copper, carbon, etc.

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

The electrolytic reduction of nitrates may also be made to yield nitrites under suitable conditions.[2]

4. A solution containing nitrous acid may be prepared by the reduction of nitric acid by nitric oxide.

$$HNO_3 + 2NO + H_2O \rightleftharpoons 3HNO_2.$$

[1] Divers, *Chem. Soc. Trans.*, 1899, **75**, 85.
[2] Müller and Spitzer, *Zeitsch. Elektrochem.*, 1905, **11**, 917.

Properties. Nitrous acid forms, in aqueous solution, a very unstable blue liquid, which rapidly loses its colour on standing, leaving only nitric acid in the solution. This is not due to atmospheric oxidation, since nitrous acid is oxidized only very slowly by air or oxygen.

The decomposition may be represented by the equation

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

Its formation and decomposition can be demonstrated quite readily by dropping a few spots of liquid nitrogen trioxide (or tetroxide) into an excess of water, when a transient blue coloration is produced, and colourless bubbles of gas arise which turn brown on bursting at the surface, showing them to consist of nitric oxide.

Rây, Dey, and Ghosh [1] find that the decomposition of nitrous acid is apparently unimolecular. The maximum concentration of the acid in water, obtainable at 0° C., was 0·185 N.

Veley [2] considers that the equation

$$3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O$$

represents the reaction only when the solution is sufficiently dilute and the temperature low. With concentrated solutions and at higher temperatures, the changes seem to be much more complicated, and it is probable that the reaction

$$2HNO_2 = N_2O_3 + H_2O$$

assumes an importance under these conditions.

Saposchnikoff [3] has investigated the decomposition reaction and determined the equilibrium constant. He found the reaction to be monomolecular and the equilibrium constant was dependent on the concentration of the nitric acid present.

The values of the equilibrium constant were of the same order, but far from constant, seeming to indicate that in addition to the above reaction, the direct decomposition of nitrous acid to nitrogen trioxide may occur.

The reaction was also examined by saturating nitric acid

[1] *Chem. Soc. Trans.*, 1917, **111**, 413.
[2] *Proc. Roy. Soc.*, 1893, **52**, 27, 54.
[3] *Chem. Zentr.*, 1900, ii., 708; 1901, ii., 1330.

with nitric oxide. The solubility of nitric oxide in various concentrations of nitric acid is shown in Fig. 8.

The reaction takes some 25 hours for a concentration of nitric acid of 0·05 N, while it is complete in a few minutes with an acid of sp. gr. 1·4. This fact is of considerable importance in the cycle of reactions in an absorption system.

The equilibrium has also been investigated by Lewis and Edgar [1] by conductivity determinations. They found also

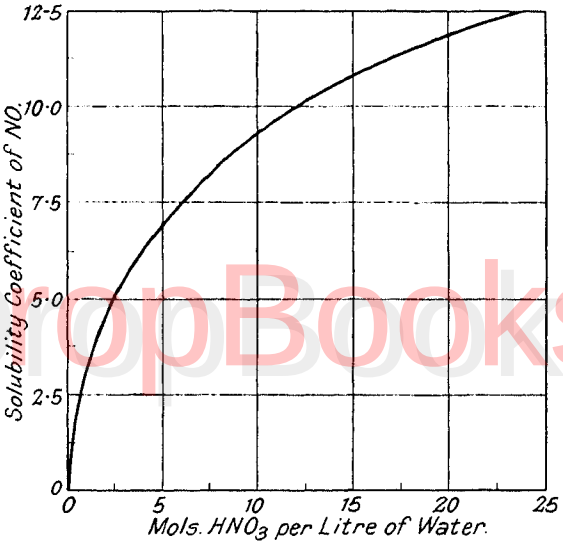

FIG. 8.—Variation of Solubility of NO in different Concentrations of Nitric Acid.

Compiled from the results of Saposchnikoff, *Chem. Zentr.*, 1908, II., 1230.

an apparent change in the equilibrium constant, with the concentration of nitric acid.

Briner and Durand [2] studied the reversible reactions represented by the equations

$$3HNO_2 \rightleftharpoons 2NO + H_2O + HNO_3$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$$

within wide limits of temperature and pressure, and showed

[1] *J. Amer. Chem. Soc.*, 1911, **33**, 292.
[2] *Compt. rend.*, 1912, **155**, 582, 1495.

that so far as the first reaction was concerned, an increase in pressure of nitric oxide, or a decrease in temperature, favoured the formation of nitrous acid, as would be expected. Veley[1] has also examined the reaction, and finds that at equilibrium the ratio of nitric to nitrous acid

$$\frac{HNO_3}{HNO_2} = 15{\cdot}5.$$

The factors influencing the decomposition of nitrous acid in aqueous solution have been examined in detail by Knox and Reid,[2] who determined the influence of such factors as surface and agitation, excess of air, temperature, and presence of nitric acid. Their results are of particular importance from the point of view of absorption practice, since the factors they examine are such as would operate in practice.

The curves shown in Figs. 9, 10, and 11 illustrate the general results obtained, and show that the factors which accelerate the decomposition of nitrous acid are such as – a large surface, agitation, the presence of excess of air, increase of temperature, etc.

The effect of the presence of nitric acid, which is of particular interest in absorption practice, shows that the initial rate of decomposition of nitrous acid is accelerated by the presence of nitric acid, but as the decomposition proceeds the velocity becomes less, and in its final stages seems to be slightly slower than the velocity in the absence of nitric acid, with similar concentrations.

The importance of agitation and surface is also very apparent, and indicates clearly that under the ordinary conditions applying in absorption systems, the rate of decomposition of nitrous acid must be very rapid.

Nitrous acid is completely oxidized to nitric acid by the common oxidizing agents. Potassium permanganate, chromic acid, hydrogen peroxide, ozone, etc., are all effective in this respect.

Nitrous acid may also function as an oxidizing agent. For example, stannous chloride, hydrogen sulphide, and sodium amalgam will all reduce nitrous acid to nitric oxide, nitrous

[1] *Chem. Soc. Trans.*, 1917, **111**, 415.
[2] *J. Soc. Chem. Ind.*, 1919, **38**, 105T.

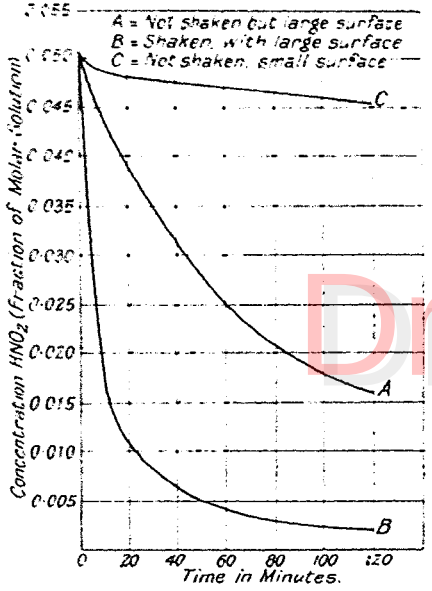

FIG. 9.—Effect of Shaking and of Surface on Decomposition of Nitrous Acid.

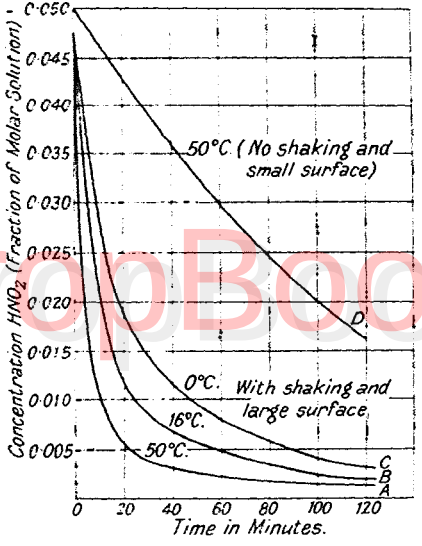

FIG. 10.—Effect of Temperature on Decomposition of Nitrous Acid.

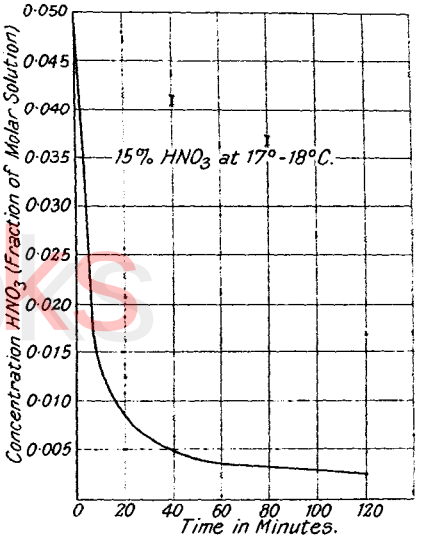

FIG. 11.—Decomposition of Nitrous Acid in the presence of Nitric Acid.

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Knox and Reid, *J. Soc. Chem. Ind.* 1919. **28**, 105T.

oxide, hyponitrous acid, and even to nitrogen. Hydrazine also reacts quantitatively with nitrous acid, giving a mixture of nitrous oxide and ammonia, while urea yields carbon dioxide and nitrogen.

$$N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O$$
$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

When added to a solution of potassium iodide, nitrous acid causes an immediate liberation of iodine, a reaction which may conveniently be used for the estimation of the acid. A number of organic colouring matters are also bleached quite readily by nitrous acid, the common indicators, litmus, methyl orange, and phenolphthalein, being rapidly decolorized. This property of nitrous acid causes difficulty in the titration by

Thermochemistry. The decomposition of nitrous acid is an endothermic reaction. The heat of formation from nitrogen trioxide is as follows :—

N_2O_3, aq. = − 6,820 cal.
2NO, O, aq. = − 36,330 cal.
N, O_2, H, aq. = + 30,770 cal.
NO, O, H, aq. = + 52,345 cal.

Briner and Durand[1] have shown that the decomposition of nitrous acid in dilute solution is attended with the absorption of 18·4 cals.

$$3HNO_2 = 2NO + H_2O + HNO_3 - 18{\cdot}4 \text{ cals.}$$

Heat of neutralization (with baryta) = 10,600 cals.

The chief methods for the estimation of nitrous acid are given in Chapter IX. The acid or its salts may be detected in aqueous solution by a number of very sensitive colour reactions.

The most useful substances in this connection are :—

1. Metaphenylenediamine, which gives a deep brown coloration with small quantities of nitrites or nitrous acid.
2. Potassium iodide and starch solution, which gives a deep blue coloration.
3. Griess Ilosvay reagent (sulphanilic acid and β-napthylamine), which gives a rose-pink coloration with nitrites. This test is sensitive to approximately 1 part of nitrite per million parts of water.

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Nitric Acid, HNO_3

Nitric acid is found in nature in combination with a number of metals as nitrates, the commonest being those of sodium, potassium, calcium, and magnesium. Electric discharges in the atmosphere, and the nitrifying bacteria in the soil, are two important contributory causes to its natural production.

The present largest natural deposits occur in Chile as sodium nitrate and in Bengal as potassium nitrate.

Preparation. There are at present two main methods of

[1] *Compt. rend.*, 1912, **155**, 1495.

production of nitric acid. The first is the old process of manufacture from sodium nitrate and concentrated sulphuric acid.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

The second general method of production consists in the fixing of atmospheric nitrogen, in such a form that it can finally be recovered as nitric acid. Such methods are divisible again into direct and indirect methods. The direct consist of processes involving the use of high temperatures which are mainly obtained by the electric arc—but may also be produced by other methods such as explosion, surface combustion, and so on.

The indirect methods involve the production of ammonia, and its subsequent oxidation to oxides of nitrogen, and the conversion of these oxides to nitric acid.

The ammonia may be synthesized directly in the presence of a catalyst from nitrogen and hydrogen, or it may be obtained from cyanamide, as in the Frank-Caro process, or from aluminium nitride as in Serpek's process, or from cyanides as in Bücher's process. Many modifications of the "pot" process have also been put forward, these consisting mainly in the decomposition of sodium nitrate by substances other than sulphuric acid, with a view to the ultimate recovery of caustic soda as a by-product. Such substances include silica, ferric oxide, manganese dioxide, etc. For details of these and other methods the reader is referred to standard works on the manufacture of nitric acid.

Ordinary commercial nitric acid contains only about 70 per cent. HNO_3, and as most of the acid used in this country is obtained by the pot process it usually contains small quantities of hydrochloric acid, iodine, iron salts, and traces of sulphuric acid as impurities. Unless the acid has been "bleached" by air-blowing, it will also contain varying quantities of dissolved nitrogen tetroxide. By distillation of nitric acid with concentrated sulphuric acid in a current of carbon dioxide 98–99 per cent. HNO_3 can be obtained.

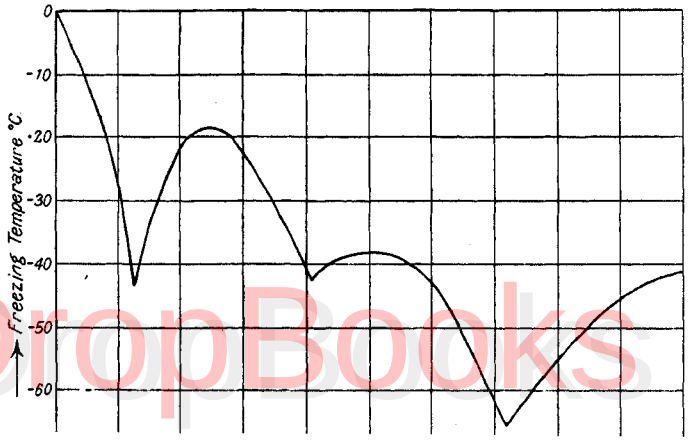
Küster and Munsch [1] obtained an acid of 99·4 per cent. HNO_3 by freezing an acid containing 98 per cent. HNO_3.

[1] *Zeitsch. anorg. Chem.*, 1905, **43**, 350.

Veley and Manley [1] state that they have obtained pure anhydrous nitric acid by distillation of 98–99 per cent. HNO_3, but this is not borne out by the work of Küster and Munsch,[2] who state that 100 per cent. nitric acid is only capable of existence at $-41°$ C., when it forms a snow-white solid. Above this temperature it decomposes readily in sunlight.

The freezing-point curve of nitric acid has been investigated by a number of workers.[3]

The curve (Fig. 12) constructed from the values of Küster and Kremann shows two maxima at $-18{\cdot}5°$ and at $-38°$,



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approximately 68 per cent. HNO_3 of sp. gr. 1·414 at 15·5° C.

The boiling-points of aqueous nitric acid have been determined by Pascal[1] and by Creighton and Githens.[2] The results in the two cases differ slightly. The curve plotted from the results of Creighton and Githens is shown in Fig. 13, the curve obtained by Pascal for the boiling-points at 760 mm. being shown superimposed on the top curve.

The acid of maximum boiling-point is clearly indicated at a concentration of about 68 per cent. HNO_3. As the concen-

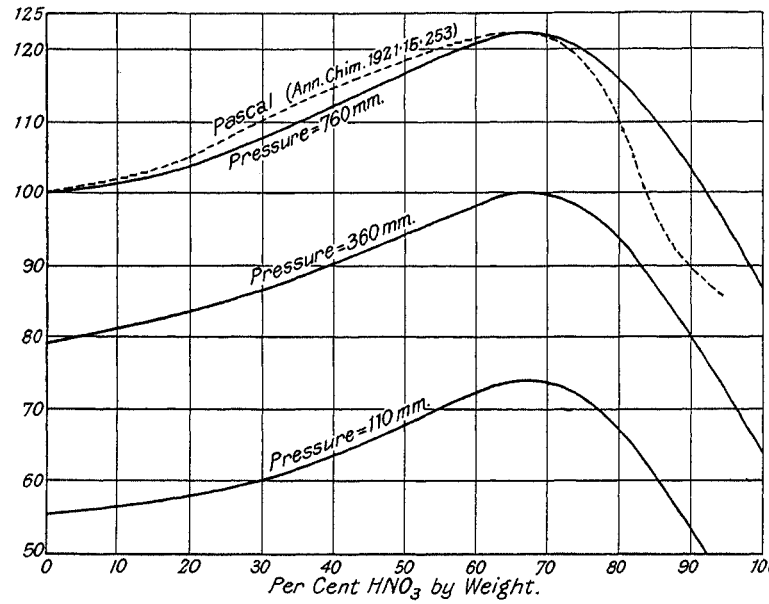

FIG. 13.—Boiling-points of Aqueous Nitric Acid at different Pressures.
Creighton and Githens, *J. Frankl. Inst.*, 1915, **17**, 161.

tration of nitric acid increases beyond this point, the boiling-point of the acid falls rapidly to 86° C.

The constant boiling nitric acid is not a compound, its composition varying with the pressure, though not very appreciably, as is shown by the following table compiled from the results of Roscoe[3] and Creighton and Githens.[4]

[1] *Ann. Chim.*, 1921, **15**, 253.
[2] *J. Frankl. Inst.*, 1915, **17**, 9, 161.
[3] *Annalen*, 1860, **116**, 203. [4] *l.c.*

TABLE 7

Pressure in mm.	Concn. of Nitric Acid per cent.	B.P. deg. Cent.
110	66·80	74·2
360	67·15	89·9
735	68·00	120·5
760	68·18	121·7
1,220	68·6	—

Vapour Pressure. The vapour pressures of nitric acid solutions of different concentrations have also been determined by Creighton and Githens.[1] The curve plotted from their results is shown in Fig. 14.

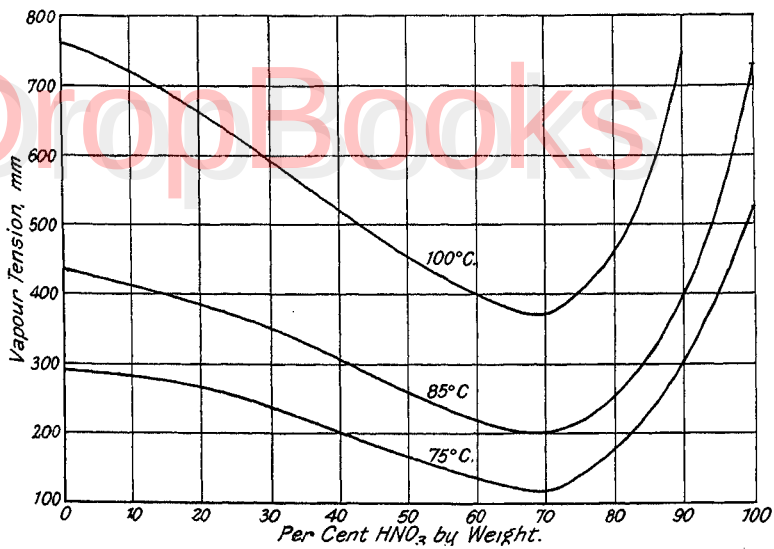

FIG. 14.—Vapour Tension of Aqueous Nitric Acid at different Temperatures.
Creighton and Githens, *l.c.*

It will be noticed that the minimum value occurs with an acid containing very nearly 70 per cent. HNO_3, this being, of course, the constant boiling mixture. The variation of the minimum vapour pressure mixture with the pressure is very slight. The composition of the vapour from various concen-

[1] *l.c.*

trations of nitric acid has been determined by Pascal,[1] who obtained the results shown in the following table.

TABLE 8

Pressure = 760 mm.

Concn. of Nitric Acid. Per cent. HNO_3.	Concn. of Nitric Acid in the Vapour at the B.P.	Concn. of Nitric Acid. Per cent. HNO_3.	Concn. of Nitric Acid in the Vapour at the B.P.
24·2	2·1	75·1	91·5
33·0	5·9	79·7	96·7
49·8	19·8	84·6	97·4
61·0	41·0	89·6	99·4
68·4	68·4	95·4	99·6
70·1	74·0		

Creighton and Githens have also determined the boiling-point of absolute nitric acid, 99·79 per cent. HNO_3, at different pressures. Their results, expressed graphically, are shown in Fig. 15. The curve also gives the saturated vapour pressure (total) at the different temperatures shown.

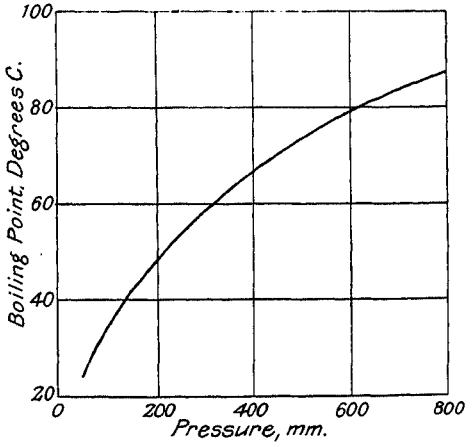

FIG. 15.—Boiling-points of Nitric Acid (99·79 per cent. HNO_3) at different Pressures.
Creighton and Githens, *l.c.*

Pure nitric acid cannot be distilled without decomposition, the acid decomposing into oxides of nitrogen and free oxygen, to an extent depending on the temperature of distillation. The following figures are given by Volney (1898) for the decomposition

$$2HNO_3 = N_2O_3 + O_2 + H_2O.$$

[1] *Ann. Chim.* 1921, **15**, 253.

TABLE 9

Temperature; deg. Cent.	Percentage Decomposition.
86	9·53
100	11·77
130	18·79
160	28·96
190	49·34
220	72·07
250	93·03
256	100·00

This decomposition constitutes a difficulty in the determination of the boiling-point of nitric acid, and the results of Creighton and Githens are vitiated to some extent by this factor, as pointed out by Pascal.

It is evident, also, that dry sodium nitrate and concentrated sulphuric acid will not give the highest concentration of nitric acid unless the temperature is kept low. It is well known in practice that a continuous decomposition of nitric acid to oxides of nitrogen occurs throughout the distillation of nitre and sulphuric acid in the pot process (see Fig. 16). When concentrated nitric acid is mixed with water the temperature rises, but a contraction in volume takes place.

The densities of various concentrations of nitric acid have been determined by Lunge and Rey [1] and by Veley and Manley.[2]

The following table shows some of the values obtained by

TABLE 10

Concn. HNO_3 per cent.	Dens. at 15°/4°.	Concn. HNO_3 per cent.	Dens. at 15°/14°.
0·10	1·00	47·49	1·30
8·99	1·05	55·79	1·35
17·11	1·10	65·30	1·40
24·84	1·15	77·28	1·45
32·36	1·20	94·09	1·50
39·82	1·25	99·67	1·52

[1] *Zeitsch. angew. Chem.*, 1891, 4, 165. [2] *l.c.*

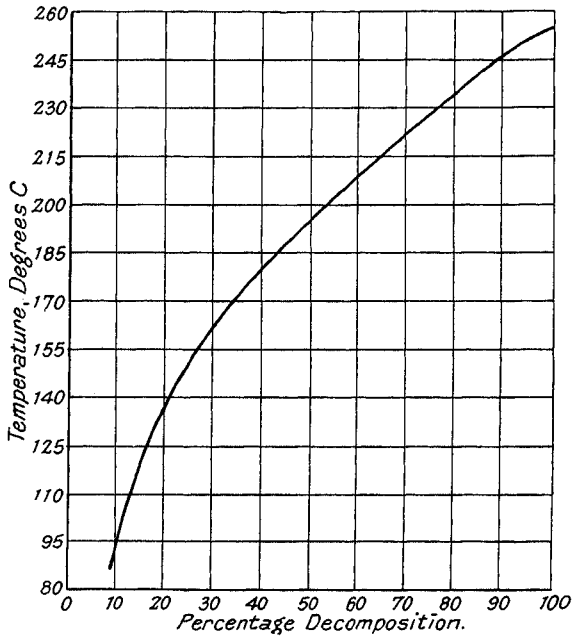

FIG. 16.—Decomposition of Nitric Acid with Rise in Temperature.
Volney, 1898.

Lunge and Rey—for other values the reader is referred to Lunge's *Technical Chemist's Handbook*.

Nitrogen tetroxide is very appreciably soluble in nitric acid and has a marked effect upon the density of the latter.

The following table, taken from the results of Lunge and

TABLE 11

Per cent. (by wt.) N_2O_4 present.	Density observed.	Per cent. (by wt.) N_2O_4 present.	Density observed.
0·25	1·4965	8·00	1·5492
1·00	1·4990	9·00	1·5560
2·00	1·5065	10·00	1·5620
3·00	1·5140	11·00	1·5690
4·00	1·5212	12·00	1·5745
6·00	1·5282	12·75	1·5795
7·00	1·5425		

Marchlewski,[1] shows the effect of nitrogen tetroxide in increasing the density of concentrated nitric acid. The original nitric acid used had a density of D_4^{15} 1·4960.

Saposchnikoff [2] has examined the vapour pressures of nitric acid mixed with sulphuric acid. The results of Pascal, and Creighton and his co-workers on this point, are given in Chapter VII.

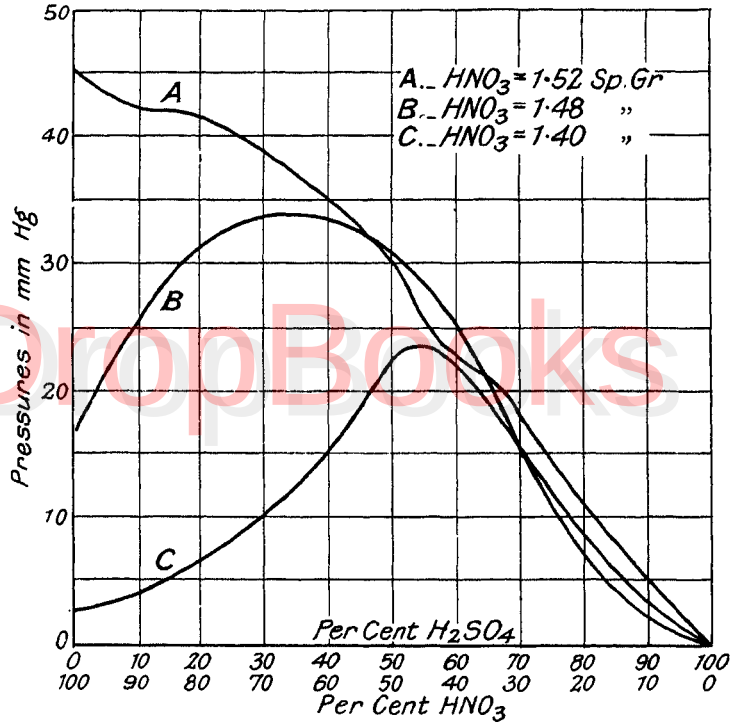

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FIG. 17.—Vapour Pressures of Mixtures of Nitric and Sulphuric Acids.
Saposchnikoff, *Zeitsch. physikal. Chem.*, 1904, 49, 697; 1905, 53, 225.

Saposchnikoff found that the maximum vapour pressure for nitric acid of sp. gr. 1·40, mixed with pure monohydrate sulphuric acid, occurs with a mixture containing 45 per cent. HNO_3, the vapour pressure being 23·5 mm.

For nitric acid of sp. gr. 1·478, the maximum occurs at 67 per cent. HNO_3, when the vapour pressure is 34 mm. A

[1] *Zeitsch. angew. Chem.*, 1892, 5, 330.
[2] *Zeitsch. physikal. Chem.*, 1905, 53, 225.

pure nitric acid of this specific gravity (1·478) has a vapour pressure of 16·6 mm., and on addition of sulphuric acid the vapour pressure increases until the maximum of 34 mm. stated above is reached. On further addition of sulphuric acid, the vapour pressure becomes equal to that of a nitric acid of sp. gr. 1·5 and then gradually falls.

The analysis of the vapour shows that, for mixtures containing 10 per cent. to 30 per cent. HNO_3, it consists of pure monohydrate. With further increase in concentration, the nitrogen content of the vapour rises (up to 24 per cent. N_2), this probably being due to the decomposition of the nitric acid by the sulphuric acid.

Thermochemical Data of Nitric Acid

The heat of formation of nitric acid has been determined by Thomsen [1] with the following results:—

$$H, N, O_3 = HNO_3\ (liq.) + 41{,}510 \text{ cal.}$$
$$NO, O_2, H = HNO_3 + 63{,}085 \text{ cal.}$$
$$NO_2, O, H = HNO_3 + 43{,}515 \text{ cal.}$$
$$\tfrac{1}{2}N_2O_4, O, H_2O = HNO_3 + 18{,}670 \text{ cal.}$$

Berthelot [2] gives the following figures:—

$$H, N, O_3 = HNO_3\ (gas) + 34{,}000 \text{ cal.}$$
$$= HNO_3\ (liq.) + 41{,}600 \text{ cal.}$$
$$= HNO_3\ (solid) + 42{,}200 \text{ cal.}$$
$$= HNO_3\ (dissolved) + 48{,}800 \text{ cal.}$$

The heat of dilution of nitric acid is as follows [3]:—

1 mol. of nitric acid dissolving in m mols. of water giving

when m = 0·5	2,005 cal.	when m = 5·0	6,665 cal.
1·0	3,285 ,,	6·0	6,980 ,,
1·5	4,160 ,,	8·0	7,220 ,,
2·0	—	10·0	7,318 ,,
2·5	5,276 ,,	20·0	7,458 ,,
3·0	5,710 ,,	40·0	7,436 ,,
4·0	—		

Other observers give the heat of solution as 7,580 cal.

[1] *Ber.*, 1879, **12**, 2062.
[2] *Compt. rend.*, 1880, **90**, 779. [3] Landolt.

The specific heats of nitric acid, due to Marignac[1] and Thomsen, are shown in the following table:—

TABLE 12

Per cent. HNO_3	3·4	12·3	58·3	3·4	15·0	26·0
Specific heat	0·9618	0·8752	0·6651	0·963	0·849	0·768
Temperature at which determination was made	21°–52° C. Marignac			18° C. Thomsen		

The heat of neutralization of nitric acid with caustic soda = 13,680 cal. and with caustic potash 13,770 cal.

Nitric acid is a strong oxidizing agent, and is itself reduced in such reactions to a number of products which include nitrous acid, nitrogen tetroxide, nitric oxide, nitrous oxide, ammonia, nitrogen, and hydroxylamine. For example iodine is oxidized to iodic acid with the production of nitric oxide,

$$10HNO_3 + 3I_2 = 6HIO_3 + 10NO + 2H_2O,$$

phosphorus to phosphoric acid, and sulphur to sulphuric acid.

Nitric acid is readily reduced by sulphur dioxide, some nitrous oxide being formed. If sulphur dioxide is passed through fuming nitric acid until the liquid becomes syrupy, crystals of nitrosyl sulphuric acid (Chamber crystals) readily separate on standing. The reaction offers a convenient method of preparing nitrosyl sulphuric acid.[2]

$$SO_2 + O_2N{\cdot}OH = SO_2\begin{matrix}OH\\ ONO\end{matrix}$$

By the addition of hydrochloric acid to concentrated nitric acid, a solution is formed containing nitrosyl chloride, and chlorine is slowly liberated. The solution is known as aqua regia

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2.$$

If the nitric acid contains less than approx. 50 per cent.

[1] *Annalen*, 1872, 8, 335.
[2] Weber, *Pogg. Ann.*, 1861, 341.

HNO_3 no nitrosyl chloride is produced, it being decomposed in the dilute solution according to the equation

$$NOCl + H_2O = HNO_2 + HCl.$$

Nitric acid may be reduced electrolytically to give a variety of products which include nitrous acid, hydroxylamine, ammonium nitrate, etc. The reduction of nitric acid has been investigated very completely by Freer and Higley, whose

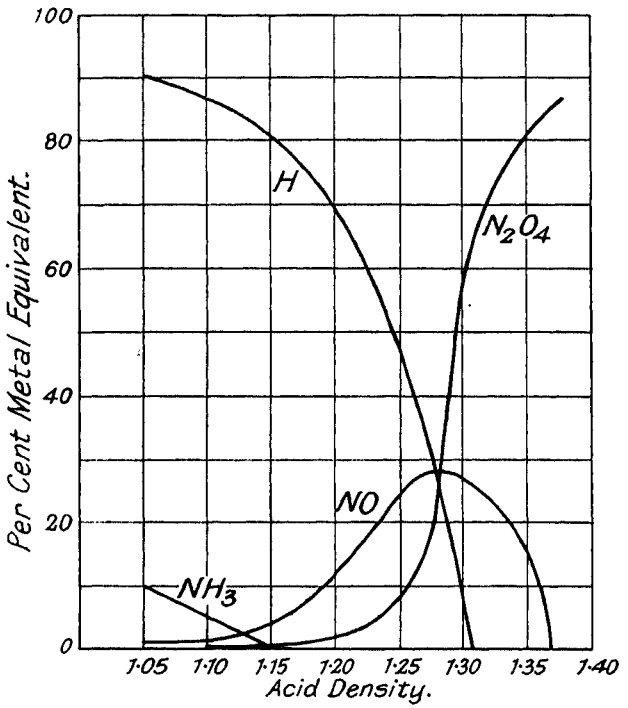

FIG. 18.—Electrolytic Reduction of Nitric Acid.
Freer and Higley, *Amer. Chem. J.*, 1893-1899, **15-21**.

results are published in the *American Chemical Journal* (1893–99).

Fig. 18 shows their results graphically. It is important to notice the absence of ammonia (i.e. ammonium nitrate) as a reduction product as the concentration of the nitric acid increases. The amount of nitric oxide produced shows a maximum value for an acid of sp. gr. between 1·25 and 1·30.

The electrolysis of more concentrated acids yields almost exclusively nitrogen tetroxide.

The conductivity of nitric acid has been examined by Veley and Manley,[1] whose results are shown in Fig. 19, the acid showing a maximum conductivity containing nearly 35 per cent. HNO_3. It is important to notice the rapid decrease in conductivity when the acid contains more than 55–60 per cent. HNO_3.

The conductivity of mixtures of nitric acid and sulphuric acid has been determined by Saposchnikoff.[2] The nitric acid

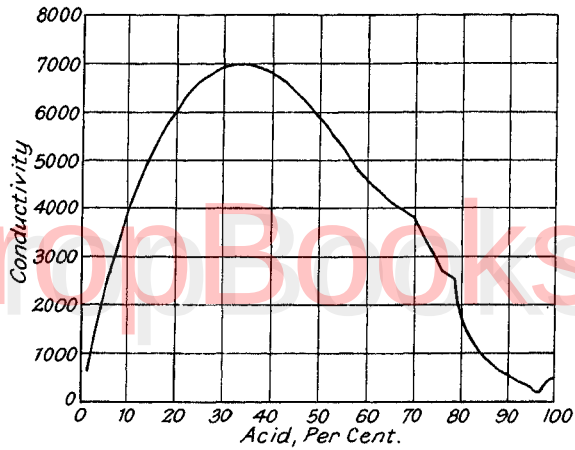

FIG. 19.—Conductivity of Nitric Acid at 15° C.
Veley and Manley, *Phil. Trans.*, 1898, 191A, 365.

used had a sp. gr. = 1·40, and the sulphuric acid was pure monohydrate. The curve (Fig. 20) shows a minimum with a mixture containing 60 per cent. of sulphuric acid and 40 per cent. of nitric acid. It should be observed also that the conductivity of such mixtures is relatively small, a fact which is of importance in considering suggested processes for the electrolytic concentration of nitric acid in the presence of sulphuric acid.

FUMING NITRIC ACID

When nitrogen tetroxide is led into concentrated nitric acid, or when a small quantity of water is added to liquid

[1] *Phil. Trans.*, 1898, **191A**, 365. [2] *l.c.*

nitrogen tetroxide, a red, fuming liquid with powerful oxidizing properties is produced. It may also be prepared by adding kieselguhr saturated with formaldehyde to concentrated nitric acid.[1]

In commerce the term fuming nitric acid is often used to indicate nitric acid containing 90–95 per cent. HNO_3, the common commercial products containing only 70 per cent. HNO_3. Fuming nitric acid, however, is a more reactive

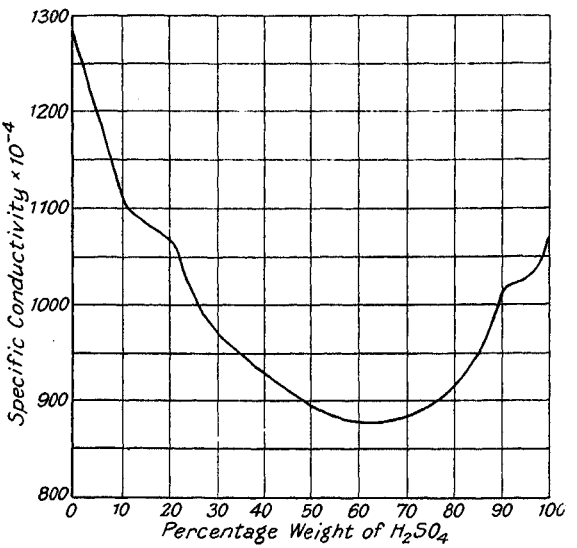

FIG. 20.—Conductivity of Mixtures of Nitric and Sulphuric Acids. Saposchnikoff, *Zeitsch. physikal. Chem.*, 1905, **53**, 231.

substance, in general, than a pure nitric acid containing the same percentage of HNO_3. This is due to the catalytic effect of the nitrous acid present, and is particularly marked in the action of nitric acid on metals and in a number of oxidation reactions.

PERNITRIC ACID

In connection with the electrolysis of nitric acid, Schellhaas [2] has found that some oxygen is fixed at a platinum anode,

[1] Vanino, *Ber.*, 1899, **32**, 1392.
[2] *Zeitsch. Elektrochem.*, 1908, **14**, 121.

and suggested that a pernitric acid was formed in accordance with the equations

$$2NO_3' + 2\oplus = N_2O_6$$
$$N_2O_6 + H_2O = HNO_4 + HNO_3.$$

The evidence for the existence of a pernitric acid is not at present very conclusive. Raschig [1] states that when nitrous acid in aqueous solution is oxidized by 3 per cent. hydrogen peroxide, a pernitric acid is formed in the solution.

$$HNO_2 + 2H_2O_2 = HNO_4 + 2H_2O.$$

He also states that the reaction does not take place if nitric acid is used, and finds that the reaction

$$HNO_4 + H_2O = HNO_3 + H_2O_2$$

takes place slowly at ordinary temperatures. This is in accord with the results obtained by estimating nitrous acid by oxidation with hydrogen peroxide and titrating the resulting nitric acid by ferrous sulphate after removal of the excess of hydrogen peroxide.

If anhydrous hydrogen peroxide is added to nitrogen pentoxide cooled in a freezing mixture, a substance is obtained having the properties of a typical per-acid.[2] It liberates bromine from potassium bromide and oxidizes aniline to nitroso-benzene and possibly contains pernitric acid, formed according to the equation

$$N_2O_5 + H_2O_2 = HNO_3 + HNO_4.$$

The exact constitution of pernitric acid is still a matter of doubt and the evidence for its existence is as yet inconclusive.

Action of Nitric Acid on Metals

Gmelin [3] states that most metals and non-metals are attacked by nitric acid at ordinary temperatures, some exceptions being gold, rhodium, platinum, iridium, tantalum, titanium, and silicon. The gaseous products consist mainly of nitric oxide, with smaller quantities of nitrous oxide and nitrogen, while the metal or non-metal is transformed into a nitrate, oxide, or oxyacid.

[1] *Zeitsch. angew. Chem.*, 1904, **17**, 1419.
[2] d'Ans and Friederich, *Zeitsch. anorg. Chem.*, 1911, **73**, 344.
[3] *Chemistry; English Translation*, Vol. II., 1849.

Pelouze and Frémy [1] give a number of details concerning the action of nitric acid on copper and silver. They also mention the formation of ammonia when tin is used and its non-formation with copper, silver, and mercury. This latter observation was confirmed by Brande and Taylor in 1863, who stated that ammonia is found as ammonium nitrate in the solutions obtained when nitric acid acts upon those metals which decompose water below red heat.

The earlier theories of the action of nitric acid on metals were based on the assumption that the oxide of the metal was first formed and then dissolved in unchanged nitric acid, e.g.

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO$$
$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

The recognition of the possibility, however, that hydrogen might be liberated in the solution, and so effect the reduction of the nitric acid, led to the abandonment of the theory of initial oxide formation.

Armstrong and Ackworth [2] developed this latter idea extensively by examining the effect of the concentration of nitric acid on the products obtained from such metals as copper, silver, zinc, cadmium, etc. They showed that nitric oxide was evolved in every case and was accompanied by amounts of nitrous oxide and nitrogen, which varied with the temperature and concentration of the nitric acid and with the concentration of the copper nitrate in the solution.

Veley [3] showed that copper, bismuth, silver, and mercury do not dissolve in pure nitric acid, free from nitrous acid, and that in solutions of nitrous acid and of a mixture of nitrous and nitric acid of equivalent concentrations, the metal dissolves more rapidly in the former. The solution of these four metals in nitric acid can be entirely prevented if a substance, which will destroy nitrous acid as fast as it is formed, is added to the solution. Such substances as hydrogen peroxide, potassium chlorate, urea, and ferrous sulphate are all effective in this respect. Zinc, cadmium, tin, etc., will dissolve quite readily in nitric acids to which such reagents have been added,

[1] *Traité de Chimie*, Vol. I., 1860, 351.
[2] *Chem. Soc. Trans.*, 1877, **2**, 54.
[3] *Phil. Trans.*, 1891, **182A**, 279.

and nitrous acid is not necessary to initiate the reaction. These latter metals also produce ammonia (as ammonium nitrate) when dissolving in nitric acid, while copper, silver, mercury, etc., do not. The metals may therefore be divided into two groups (Table 13) :—

(A) Those which require nitrous acid to initiate the reaction, and which do not give rise to ammonia when dissolving in nitric acid.

(B) Those which do give rise to ammonia as a reduction product, and which do not require nitrous acid to initiate the reaction.

TABLE 13

B	A
Zinc	Copper
Cadmium	Silver
Tin	Mercury
Lead	Bismuth
Aluminium	etc.
Iron	
Magnesium	
Potassium	
Sodium	
etc.	

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Such a classification was first proposed by Divers.[1] Veley showed that both classes of metals give rise to nitrous acid in dissolving in nitric acid.

Divers [2] suggested from the above classification that those metals which gave rise to ammonia caused the initial formation of hydrogen in the solution, which hydrogen reduced the nitric acid to various reduction products such as nitrous acid, nitric oxide, hydroxylamine, ammonia, etc. The following equations would then represent the reactions involved.

$$HNO_3 + 2H = HNO_2 + H_2O$$
$$HNO_3 + 4H = H_2N_2O_2 + H_2O$$
$$HNO_3 + 6H = NH_2OH + 2H_2O$$
$$HNO_3 + 8H = NH_3 + 3H_2O.$$

[1] *Chem. Soc. Trans.*, 1883, **43**, 443. [2] *l.c.*

Divers observed that hydroxylamine was produced when zinc, and also tin dissolved in nitric acid. Traces of this substance were also obtained with aluminium, cadmium, magnesium, etc.

The nitric oxide evolved might then be produced by the reaction

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

Nitrous oxide N_2O would be obtained from the decomposition of hyponitrous acid,

$$H_2N_2O_2 = N_2O + H_2O,$$

or also from the reaction

$$NH_2OH + HNO_2 = N_2O + 2H_2O,$$

while nitrogen might be produced by the interaction of ammonia and nitrous acid,

$$NH_3 + HNO_2 = N_2 + 2H_2O.$$

The reactions in the case of zinc, for example, could then be represented as follows:—

$$3\,Zn + 7HNO_3 = 3\,Zn(NO_3)_2 + NH_2OH + 2H_2O$$
$$4\,Zn + 9HNO_3 = 4\,Zn(NO_3)_2 + NH_3 + 3H_2O$$
$$4\,Zn + 10HNO_3 = 4\,Zn(NO_3)_2 + N_2O + 5H_2O$$
$$5\,Zn + 12HNO_3 = 5\,Zn(NO_3)_2 + N_2 + 6H_2O.$$

In the case of the metals, copper, silver, mercury, etc., which do not give these reduction products, Divers suggested that these metals do not replace the hydrogen directly, but that the reactions taking place are as follows:—

$$2Ag + HO{\cdot}NO_2 = Ag{\cdot}OH + AgNO_2$$
$$Ag{\cdot}OH + HNO_3 = AgNO_3 + H_2O$$
$$AgNO_2 + HNO_3 = AgNO_3 + HNO_2.$$

The nitric oxide, which is the main gaseous product in these cases, would then be the result of the decomposition of nitrous acid in the solution.

A great deal of work on the reduction products produced by the action of various metals on nitric acid has also been carried out by Freer and Higley,[1] particularly in regard to the effect of concentration, temperature, etc.

[1] *Amer. Chem. J.*, 1893–99, **15–21.**

The function of nitrous acid in initiating the reaction in the case of the metals, copper, silver, etc., is still not quite clear. If the solution pressures of the different metals be examined (Table 14) it is seen that the metals having a negative potential with respect to solutions of their salts are those which give rise to ammonia with nitric acid, while those which are positive with respect to their solutions do not give ammonia and require nitrous acid to start the reaction with nitric acid.

TABLE 14

SOLUTION PRESSURES

Negatively charged.		Positively charged.	
Sodium	− 2·7	Hydrogen	± 0
Magnesium	− 1·48	Copper	+ 0·329
Aluminium	− 1·28	Mercury (-ous)	+ 0·775
Manganese	− 1·07	Silver	+ 0·80
Zinc	− 0·770	Platinum	+ 0·86
Iron	− 0·46		
Cadmium	− 0·42		
Cobalt	− 0·3		
Nickel	− 0·25		
Tin	− 0·19		
Lead	− 0·12		
Hydrogen	± 0		

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The probability is, therefore, that in the case of metals with a higher solution pressure than hydrogen (i.e. those metals which are negatively charged with respect to their aqueous solutions), hydrogen is first liberated when the metal is put into nitric acid, with consequent reduction, varying with the temperature and concentration of the acid, and the nature of the metal.

In the case of the metals which have a lower solution pressure than hydrogen, these will be effectively polarized on putting them into a solution containing hydrogen ions. The function of the nitrous acid in initiating the reaction in such a case is therefore that of a depolarizer.

This explanation of the mechanism of the reaction is also borne out by a number of experimental observations. Mag-

nesium and very dilute nitric acid yields almost pure hydrogen. The products of the electrolytic reduction of nitric acid are also almost exactly analogous to those given by such metals as iron and zinc, etc., and since the former result is produced by hydrogen, it is reasonable to assume that the mechanism in the case of the metal is similar. The curve shown in Fig. 21 should be compared with Fig. 18 on page 61.

The non-production of ammonia in the case of the copper series gives also additional support to the hypothesis.

The action of nitric acid on metals is further complicated

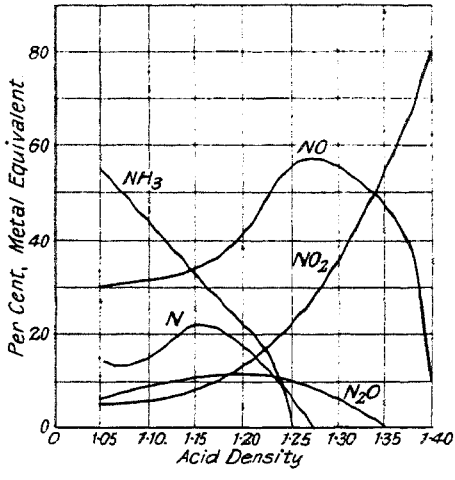

FIG. 21.—Action of Nitric Acid on Iron.

Freer and Higley, *Amer. Chem. J.*, 1893–1899, **15–21**.

by the factors of temperature and concentration, by the presence of traces of hydrochloric acid and sulphates, etc., in the nitric acid, and by the accumulation of the products of reaction in the solution.

In the case of the factor of concentration, the rate of solution of the metal usually increases up to a maximum and then falls off at higher concentrations. The composition of the gaseous and other reduction products is also appreciably changed. A reference to Figs. 18 and 21 on pages 61 and 69, summarizing Freer and Higley's results in the case of iron and nitric acid, amply illustrates this point. Armstrong

and Ackworth [1] found similarly that in the case of copper a nitric acid containing $HNO_3 : H_2O = 1 : 2$ gave a gas containing 98 per cent. nitric oxide, the remainder consisting of nitrous oxide and nitrogen. Similar results were obtained with 1 : 1 acid.

1 : 0 acid gave $NO = 54{\cdot}0\%$
$N_2O = 10{\cdot}3\%$
$N_2 = 35{\cdot}7\%$

1 : 4 acid gave $NO = 94\%$
$N_2O = 3{\cdot}5\%$
$N_2 = 2{\cdot}15\%$

while 1 : 8 acid gave $NO = 71{\cdot}89\%$
$N_2O = 20{\cdot}74\%$
$N_2 = 7{\cdot}37\%$

Again, the variation in rate of solution of the metal is illustrated in the case of lead (Fig. 22), where a maximum rate of solution occurs at 29 per cent. HNO_3. This is probably dependent in part on the solubility of lead nitrate in nitric acid, as was pointed out by Veley [2] (see Fig. 23).

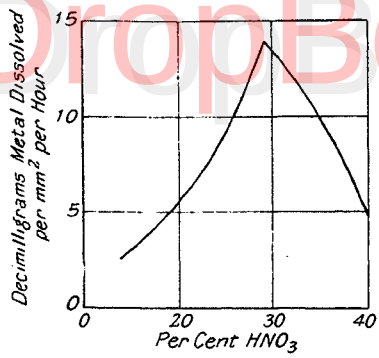

Fig. 22.—Action of Nitric Acid on Lead.
Veley, *J. Soc. Chem. Ind.*, 1891, 207.

A considerable amount of work has also been carried out on the effect of the presence of metallic nitrates, etc., on the reaction. The influence of copper nitrate has already been mentioned. Rennie [3] showed that the presence of certain salts, such as sodium nitrate, causes appreciable acceleration in the rate of solution of metals such as copper in nitric acid. Similar results have been put forward by Rây,[4] who examined the effect of sodium nitrate and manganous nitrate on the rate of solution of mercury in nitric acid. Both salts were found to accelerate the reaction, but the reaction was retarded

[1] *l.c.*
[2] *l.c.*
[3] *Chem. Soc. Trans.*, 1911, **99**, 1035.
[4] *Ibid.*, 1012.

by the presence of minute traces of ferric nitrate or ferric sulphate.

The action of alloys with nitric acid is even more complicated than in the case of the pure metals. Montemartini [1] examined the action of alloys of zinc with magnesium, aluminium, cadmium, bismuth, tin, copper, and silver, dealing mainly with the production of ammonia, by the action of the above alloys on nitric acid varying in concentration from 0·25 per cent. to 60 per cent. HNO_3, the temperature of reaction lying between 7°–10° C. In all cases it was found that the tendency to ammonia formation was very small when the acid became concentrated, the maximum amount of ammonia being obtained in general with acids of moderate concentration (approx. 40 per cent. HNO_3).

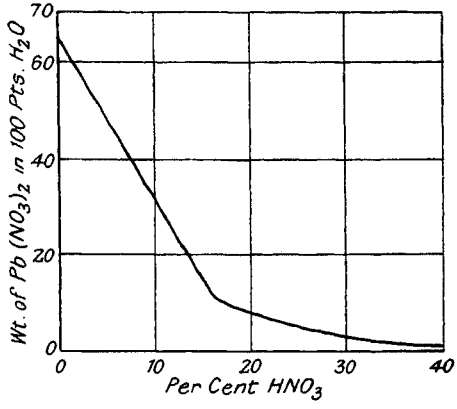

FIG. 23.—Solubility of Lead Nitrate in Nitric Acid.

Veley, *l.c.*

A great deal of work on the action of nitric acid on copper containing small percentages of arsenic, antimony, bismuth, phosphorus, lead, etc., has been carried out by Stansbie,[2] for details of which the original papers should be consulted.

The curves given in Fig. 24 indicate the peculiar protective action of small quantities of other metals and non-metals on the rate of solution of copper and on the volume of gas evolved.

The influence of small amounts of impurities on the rate of solution of metals in nitric acid is of considerable commercial importance. At the present time, almost the only available materials in which weak nitric acids can be handled are stoneware, aluminium, and various alloys of iron and silicon containing 12–20 per cent. Si, and sold under the names of tant-

[1] *Chem. Soc. Abstr.*, 1907, ii., 619.
[2] *J. Soc. Chem. Ind.*, 1906–13.

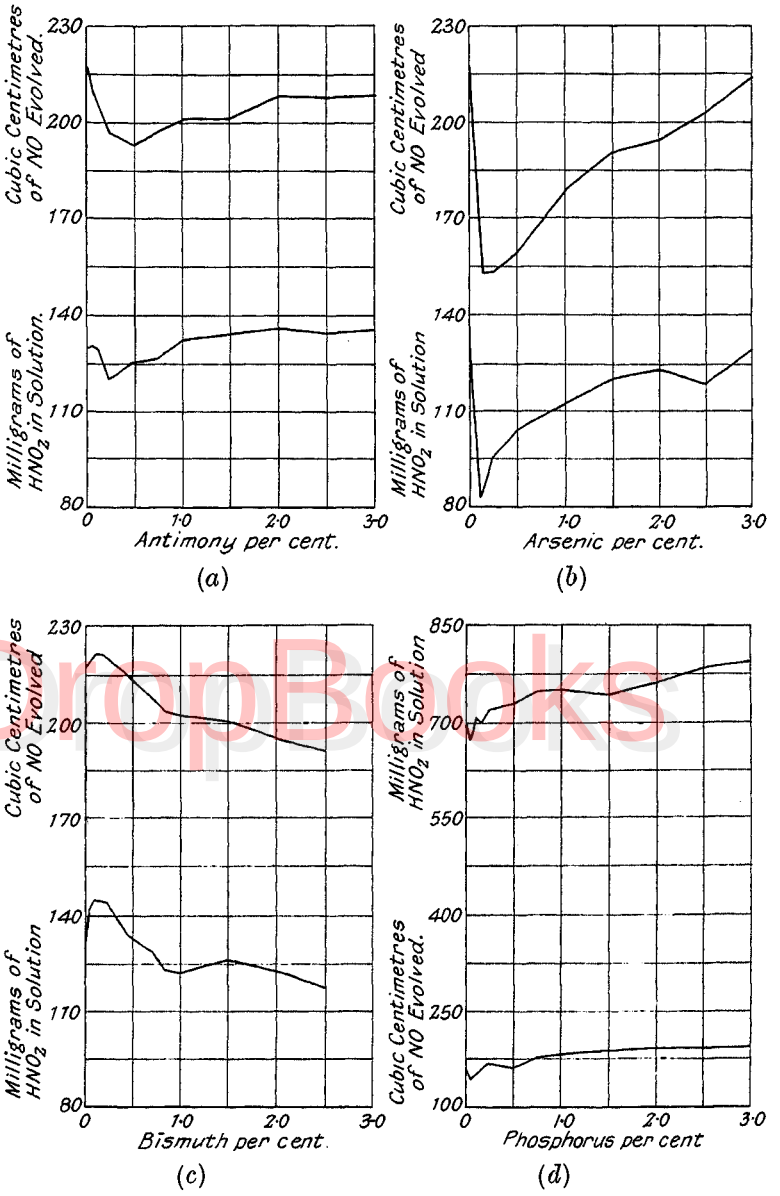

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FIG. 24.—Effect of (*a*) Antimony, (*b*) Arsenic, (*c*) Bismuth, and (*d*) Phosphorus on the Rate of Solution of Copper in Nitric Acid.

Stansbie, *J. Soc. Chem. Ind.*, 1906–1913.

iron, narki, ironac, etc. Iron is resistant to very concentrated nitric acids, but is very rapidly attacked by weak nitric acids.

Trillat [1] has examined in detail the action of nitric acid on aluminium. He found that the corrosion was much greater if the test solutions containing the acid and aluminium plates were exposed to the air, while the greatest corrosion occurred at the surface of the liquid. He found that it was impracticable to protect the aluminium by coating with paraffin, celluloid, varnish, etc., but the resistance to corrosion was increased by a preliminary heating of the metal to temperatures between 400°–500° C. This treatment, however, impairs the mechanical properties of the metal. Welded aluminium was found by Trillat to be as resistant as the untreated metal, but this is not the normal experience in the case of aluminium pipes and tanks, the weld being the first part to be attacked. The work of Seligman and Williams [2] on the action of nitric acid on aluminium is also very important. Their general conclusions were mainly identical with those of Trillat [3] and were as follows :—

1. That the temperature is a most important factor, a rise of 10° C. increasing the rate of corrosion by approximately 100 per cent.

2. The next most important factor is the concentration of the nitric acid. The most active nitric acids contained 20–40 per cent. by volume of nitric acid of 1·42 sp. gr. On the other hand nitric acid containing 94–95 per cent. HNO_3 was found to be almost without action on aluminium.

3. Impurities in the nitric acid, such as traces of sulphuric acid, increased the rate of attack. For example, 0·04 per cent. H_2SO_4 increased the rate of dissolution from 36 to 62 mgm. per 100 sq. cm. per 24 hours. Contrary to the results of Trillat, however, they found that up to 0·05 per cent. chlorine, or to 0·01 per cent., iodine, had no accelerating effect on the rate of attack.

4. Oxides of nitrogen in the nitric acid also increased the rate of attack, and if the nitric acid used was kept free from lower oxides of nitrogen, the rate of attack was considerably reduced.

5. Amorphous (unannealed) aluminium was attacked much

[1] *J. Soc. Chem. Ind.*, 1915, **34**, 874. [2] *l.c.* 1916, **35**, 665. [3] *l.c.*

more readily than the crystalline (annealed) metal, although the composition of the metal was of relatively smaller importance than is usually thought to be the case. The pure metal is, however, the most resistant to corrosion.

6. Mixed acids attack aluminium much more readily than nitric acid alone. This is contrary to the statements of Guttmann on the subject.[1]

The aluminium examined by Seligman and Williams had

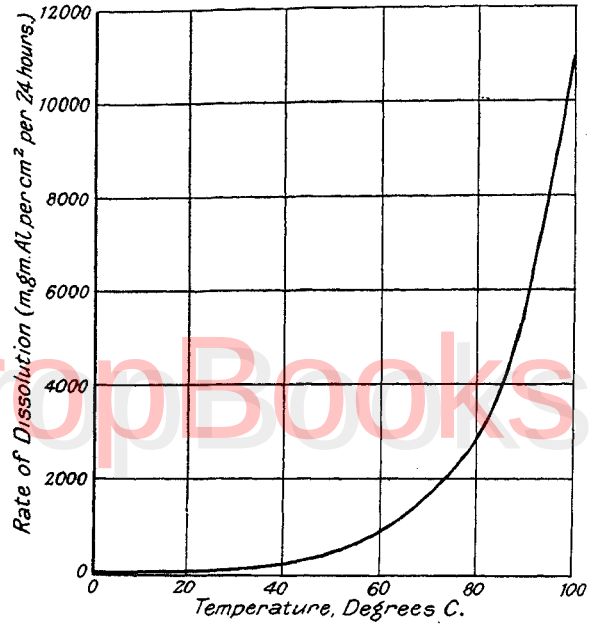

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FIG. 25.—Effect of Temperature on the Action of Nitric Acid on Aluminium.
Seligman and Williams, *J. Soc. Chem. Ind.*, 1915, **35**, 665.

the composition Al, 99·10; Fe, 0·45; Si, 0·45; Cu, 0·00 per cent. For the rate of dissolution with temperature they obtained the results shown in Fig. 25.

For the effect of concentration, the curve obtained by them is shown in Fig. 26, and indicates very clearly the maximum values with acids containing between 20–40 per cent. H_2O.

The results obtained with mixed acid made up from 98 per cent. H_2SO_4, and nitric acid of sp. gr. 1·52, have also been

[1] *J. Soc. Chem. Ind.*, 1896, **15**, 850.

expressed in the form of a curve (Fig. 27) plotted from the results of Seligman and Williams.

The curve shows a maximum at about 65 per cent. H_2SO_4 and 35 per cent. HNO_3. It also indicates that the addition of small quantities of sulphuric acid to concentrated nitric acid increases the amount of corrosion of aluminium. This is contrary to the general experience in the case of metallic iron, where the addition of approximately 5 per cent. of sulphuric to concentrated nitric acid considerably decreases the corrosive action of the latter with respect to the metal.

Some earlier work on the action of nitric acid on aluminium

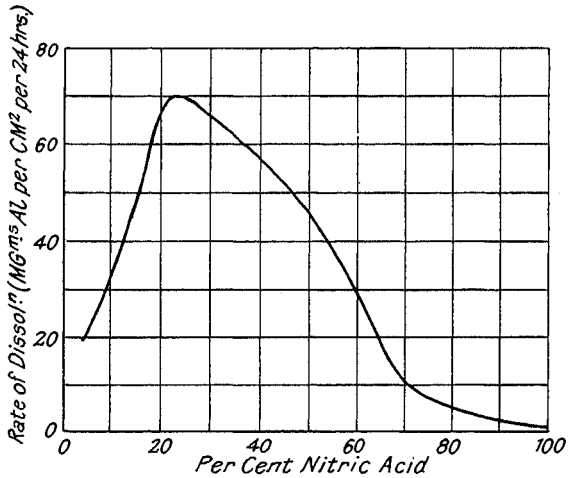

FIG. 26.—Effect of the Concentration of Nitric Acid on the Rate of Solution of Aluminium.

From the results of Seligman and Williams, *J. Soc. Chem. Ind.*, 1916.

was carried out by Lunge and Schmidt,[1] who concluded that aluminium cannot be used in the construction of apparatus for the manufacture of nitric acid.

The general conclusion to be drawn from the published work on the action of nitric acid on aluminium, is that the metal can be used with safety for nitric acid work provided that the acid is at a low temperature and either very dilute or very concentrated. In this connection, Fr. P. 451,812 of 1912 covers the use of aluminium vessels for transporting nitric

[1] *Zeitsch. angew. Chem.*, 1892, **5**, 7.

acid and specifies the use of pure metal. At the present time aluminium is widely used for the construction of air-elevator pipes for circulating weak nitric acid in absorption systems, e.g. at Notodden in Norway. It is also used in the construction of tanks for blending mixed acids, for domes and covers for acid tanks, and for the conveyance of nitric acid. In the case of tanks used for the conveyance of the acid, it is essential that these should be very carefully washed out with dilute alkaline solutions when not in use, or alternatively made quite

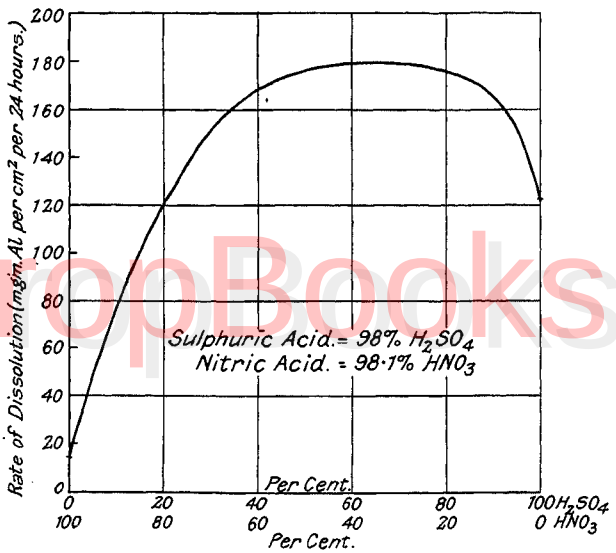

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FIG. 27.—Relative Corrosion of Aluminium by Mixed Acids at Ordinary Temperatures.

From the results of Seligman and Williams, *J. Soc. Chem. Ind.*, 1915, **35**, 665.

air-tight so as to prevent the access of moisture, since the greatest corrosion occurs where the acid is diluted in contact with a relatively large surface.

Great care is required in the use of aluminium for mixed acid work, especially as regards increase in temperature. In the author's experience aluminium domes and hoods with which nitric acid vapours come in contact are attacked very rapidly, while contact of aluminium apparatus with hot mixed acid results in complete solution of the metal within a very few minutes. With due precautions, however, aluminium can

be made reasonably useful for a number of purposes in absorption practice.

Passivity. When iron is immersed in nitric acid of sp. gr. not less than 1·25 (40 per cent. HNO_3), the iron becomes "passive" and will not precipitate copper from a solution of copper sulphate. By tapping or scratching the surface, however, the metal may be again rendered active and function in the normal way. The sp. gr. of nitric acid between 1·25–1·26 is usually known as the "passive break," owing to it being the lowest concentration which will induce passivity in iron. A very complete bibliography on passivity is given by Heathcote.[1] Recent work on the passivity of iron by Young and Hogg [2] seems to show that the passivity induced by nitric acid is due to an equilibrium between iron and nitrogen tetroxide, but owing to the reversibility of the reaction $N_2O_3 = \frac{1}{2}[N_2O_4] + NO$, it is impossible to state whether the passifying agent is nitrogen tetroxide, nitrous acid, or a mixture of both. The rate of reaction between nitric acid and iron falls off rapidly as the density rises above 1·26. A much greater degree of passivity seems to be obtained by exposing iron to nitrogen tetroxide than by treatment with nitric acid, although no gas film could be discovered on the metal.

Acid-resisting Alloys for use in handling Nitric Acid

The types of material in which nitric acid has been, and is now, handled, are somewhat numerous.

Platinum, glass, stoneware, porcelain, silica, and aluminium are examples of these materials. The development of iron-silicon alloys has opened up a new and wide field of construction in acid-resisting apparatus.

Some of the earliest work in this connection was carried out by Jouve in 1903 and later by Lennox, Pierce and Marsden in this country. An admirable account of the history of this field of discovery will be found in an article by Matignon [3] and also one by Tungay.[4]

The types of material at present in existence are all similar

[1] *J. Soc. Chem. Ind.*, 1907, **26**, 899.
[2] *J. Phys. Chem.*, 1915, **19**, 617.
[3] *Chim. et Ind.*, 1919, **2**, 11.
[4] *J. Soc. Chem. Ind.*, 1918, **37**, 87T.

in composition and general properties. In England we have tantiron made by the Lennox Foundry Co., ironac made by Messrs. Haughtons, Ltd., and narki by Messrs. Varley & Co. In America, the standard product is duriron made by the Dayton Co., Ohio. In France superneutral and métillure are types of such products. Krupps produce neutraleisen, which is now somewhat extensively used. Rossi,

FIG. 28.—Variation in Hardness of Iron-Silicon Alloys with the Percentage of Silicon.

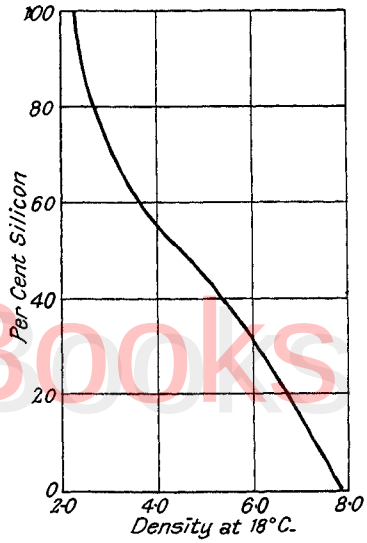

FIG. 29.—Density of Iron-Silicon Alloys.

From the results of Schwarz (*l.c.*).

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in Italy, also makes elianite for his synthetic nitric acid plant.

Guertler and Tiemann [1] have carried out an examination of the equilibrium curve between solid and liquid phases in the system Fe-Si and find that with alloys containing up to 20 per cent. silicon the crystals consist of mixed crystals of iron and a silicide of the composition Fe_2Si. The introduction of increasing quantities of silicon in alloys with iron causes very wide changes in the physical and chemical properties of the product. Density, hardness conductivity for heat and electricity all undergo systematic variation. As is often the

[1] *Zeitsch. anorg. Chem.*, 47, 163.

case, the industrial application of the product preceded the exact scientific investigation of the physical and chemical nature of the alloys. Figs. 28 and 29 show in graphic form the variation of the hardness and density of the alloys. The hardness of these alloys varies, of course, with the conditions of cooling, etc., but normally treated metal shows a maximum hardness at 7·5 per cent. silicon.[1]

Kowalke[2] has determined the variation in acid-resisting properties with the percentage of silicon in these alloys. His results in the case of 10 per cent. nitric acid were as follows, all the tests being carried out at air temperature.

TABLE 15

Per cent. Si.	Area of Test Piece, sq. cm.	Cumulative Loss per cent.		
		115 hours.	166 hours.	14 days.
2·5	8·4	20·8	48·0	53·5
3·3	11·8	13·3	21·6	22·1
7·9	11·2	8·9	11·1	11·4
9·4	7·3	5·9	8·7	8·9
11·1	10·4	2·4	3·5	3·6
12·4	13·1	2·3	4·6	4·6
13·6	11·7	0·051	0·1	0·1
14·8	6·3	0·013	0·02	0·02
16·1	11·4	0·006	0·003	0·0015
17·3	11·2	0·006	0·007	0·007
18·5	8·0	0·037	0·044	0·046
19·8	13·8	0·01	0·01	0·01

His results indicate two important facts:—

1. That the initial action very rapidly slows down, probably owing to the skin or surface of the alloy being more liable to attack.

2. The resistance to corrosion varies in a marked way with the silicon content of the alloy. The results have been expressed graphically (Fig. 30) in order to emphasize these points.

[1] Schwarz, *Ferrum*, 1914, **11**, 80, 112.
[2] *J. Amer. Electrochem. Soc.*, 1917, 206.

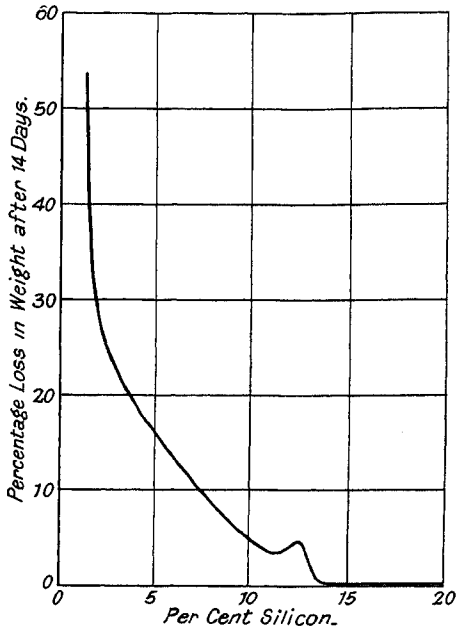

FIG. 30.—Corrosion of Iron-Silicon Alloys containing varying Percentages of Silicon. From the results of Kowalke, *J. Amer. Electrochem. Soc.*, 1917, 206.

It is also evident that when the silicon has increased beyond a certain percentage the resistance to the action of acids is very much lessened. With alloys containing 50 per cent. Si even moist carbon dioxide will cause slight decomposition. In view of the results of Kowalke and Schwarz, it is interesting to examine the analysis of some of the typical iron-silicon alloys at present on the market. Matignon [1] gives a number of analyses, many of which have been carried out by himself.

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TABLE 16

	Métil-lure.	Cian-ite I.	Cian-ite II.	Ironac.	Dur-iron I.	Duriron II.[2]	Tantiron.
Si	16·92	15·07	15·13	13·16	15·51	14–14·5	14–15
Fe	81·05	82·40	80·87	83·99	82·23	85·3–84·3	—
Mn	0·88	0·60	0·53	0·77	0·66	0·25–0·35	2–2·5
Ni	0·0	0·60	2·23	0·0	0·0	—	—
Al	0·25	„	0·0	0·0	0·0	—	—
C	0·592	„	0·82	1·08	0·83	0·20–0·60	0·75–1·25
P	0·173	„	0·06	0·78	0·57	0·16–0·20	0·05–0·10
S	0·01	„	0·03	0·05	0·01	<0·05	0·05–0·15
Ca & Mg	0·00	„	0·00	0·0	—	—	—
Density	6·71	6·87	7·14	6·71	6·44	7·00	6·86

[1] *Chim. et Ind.*, 1920, 11.

[2] The analysis of Duriron II. is due to Carnell, *J. Ind. Eng. Chem.*, 1916, 972.

FIG. 31.—Narki Castings for Nitric Acid Plant.
John Varley & Co.

It will be seen that most of the alloys contain a little manganese and also carbon. The former probably renders the metal more fusible. The presence of carbon is deleterious, since silicon carbide separates out on cooling, and graphite also forms in the mass, rendering it heterogeneous, and consequently more liable to attack by acids. So far as the acid-resisting properties of the metal are concerned, even in the case of nitric acid, there is very little left to be desired, provided that the silicon content is greater than 10 per cent. Si and less than 20–22 per cent. Si, e.g. Rossi [1] describes an acid-resisting alloy containing not less than 13–15 per cent. Si and not more than 20–21 per cent. Si, and these figures express

[1] E.P. 121, 730, 1918.

the rough limits of composition of all the present commercial alloys.

Examples of the resistivity of such alloys to the action of dilute and concentrated nitric acid are given by Matignon.[1]

TABLE 17

Alloy.	Weight in grams (approx.)	Loss in weight per hour per 100 sq. cm.	Concn. of Nitric Acid used, per cent. HNO_3.
		grams.	
Métillure	11	0·0003	52·0
„	12	0·00005	25·0
Élianite	8	0·0115	52·0
„	4	0·0113	25·0
Tantiron	4	0·00099	52·0
„	2·5	0·00256	25·0
Ironac	1·56	0·025	52·0
„	5	0·057	25·0
Duriron	8	0·00198	52·0
„	8	0·00412	25·0

Tungay[2] gives the following tests for ironac:

TABLE 18

Acid used.	Weight of Alloy in grams.	Loss after Boiling at 150° C. for		
		24 hrs.	48 hrs.	72 hrs.
		grams.	grams.	grams.
90% HNO_3 .	13·392	0·011	0·038	0·074
30% HNO_3 .	116·629	0·013	0·016	0·016

It is evident, therefore, that a metal containing about 16 per cent. Si is exceedingly resistant to nitric acid.

The composition of acid-resisting ferro-silicon alloys varies somewhat widely, especially in the amounts of other metals present.

Recent patents have been put forward covering the addition of small quantities of molybdenum and vanadium, which

[1] *l.c.* [2] *l.c.*

metals are stated to confer greatly improved acid-resisting properties.

It must be concluded, however, that the compositions used up to the present are not based upon any very scientific data so far as the presence of metals other than iron and silicon are concerned. Provided that the proportions of iron and silicon present lie between the prescribed limits, however, a metal is obtained which is almost perfectly acid-resisting from an industrial point of view. A good deal of experimental

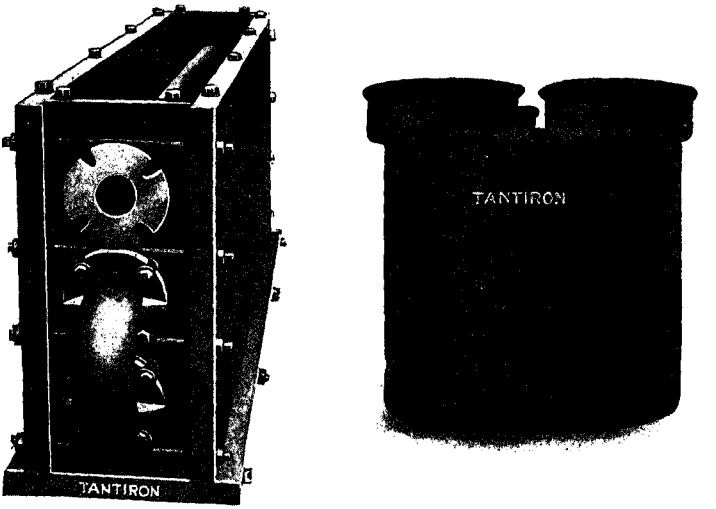

FIG. 32.—Tantiron Castings.
Lennox Foundry Co.

work still remains to be done on the effect of the addition of manganese, nickel, aluminium, etc., and the possibility of being able to decrease the necessary silicon content in this way.

It is obvious that the acid-resisting properties of these alloys have been gained at a very great sacrifice in working properties. The great difficulties in the way of the development of these alloys have lain in their manipulation and not in their lack of resistance to acids. They are all very hard and brittle, and not very fluid near their melting-points, which lie around 1,200° C. On cooling, a relatively large contraction occurs, being about three times that of ordinary cast iron. This necessitates considerable care in casting, and in many

cases a special design must be used for particular types of vessels. For example, all joints in pipe-work and reaction vessels must be formed either by means of flanges or by socket and spigot, since the metal is too hard to screw or to take a screwed thread. Similarly sharp corners have to be avoided. Ordinary machining of the metal is impossible and face-grinding has to be resorted to for obtaining approximately true surfaces.

Much difficulty is experienced also owing to the porosity of the material. In the author's experience pipe-lines, blowing mains, etc., constructed in such materials are likely to cause trouble when the air pressure reaches 30–40 lb. per square inch—acid being forced in patches right through the wall of the pipe. There is no acid-resisting iron at present on the market which could safely be recommended for the construction of vessels required to be worked at internal pressures greater than 50–60 lb. per square inch, unless the vessels are reinforced outside by cast-iron shells. In the construction of acid cocks the brittleness of the metal is liable to cause trouble and is often dangerous. Such plug cocks require very careful handling.

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The conductivity for heat of these alloys is about ten times greater than that of the industrial rival—stoneware.

Tungay [1] gives an interesting table of comparison between ordinary pig-iron and acid-resisting iron.

TABLE 20

	Ordinary Pig Iron.	Acid-resisting Iron.
Density	7·3	6·8
Tensile strength (tons sq. in.)	9–10	6–7
M.p.	1,150° C.	1,200° C.
Hardness (relative)	24	35
Heat conductivity	10	8
Electl. resistance	8	10
Contraction per ft. in casting	$\frac{1}{3\frac{1}{2}}$	$\frac{9}{3\frac{1}{2}}$
Crushing strength 1 in. cubes	40 tons	34 tons

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 87T.

The application of the electric furnace in recent years to the manufacture of the alloys, particularly by Rossi in Italy, has enabled a more satisfactory commercial product to be obtained.

In spite of the many difficulties of the materials, however, a great deal of exceedingly useful and durable chemical plant has been constructed, and this has only been made possible by the enterprise of the firms concerned in its development.

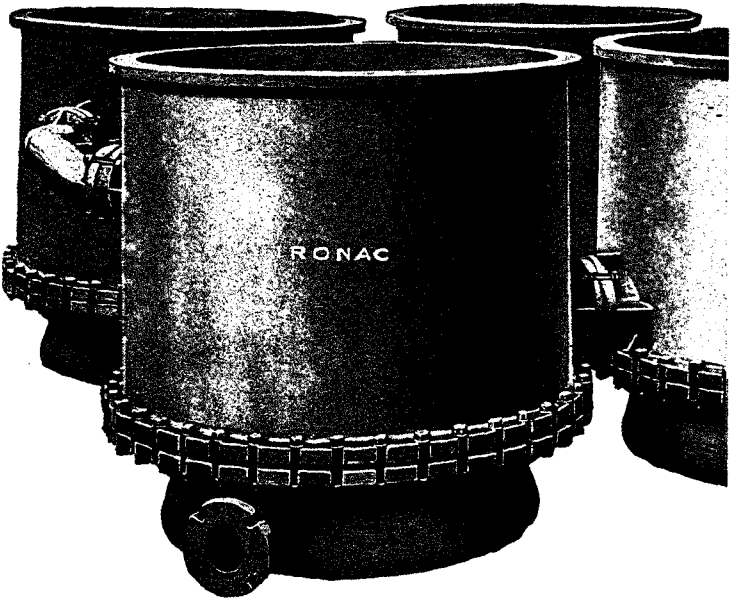

FIG 33.—Ironac Pots for Weak Acids.
Haughton's Patent Metallic Packing Co., Ltd.

Illustrations of some of the various types of apparatus which can now be made are shown in Figs. 31, 32, and 33. These iron-silicon alloys are particularly useful for nitric acid work, and almost every kind of plant for acid work has been constructed. There is little doubt that with improvement in the working properties of such alloys, they will constitute the most useful constructive material for all types of acid-proof structures.

So far as acid-resisting metals are concerned, these iron-

silicon alloys at present occupy almost undisputed possession of the industrial market in the case of plant for use with nitric acid. For sulphuric acid, lead, and its alloy regulus metal, are in greater use than iron-silicon compositions. Regulus is particularly useful for valves, as it will adapt itself to the shape of the seating. On the other hand, it is a "soft" alloy and is not desirable for the construction of moving parts.

Several other acid-resisting alloys have been suggested in recent years, but do not seem to have been developed industrially to any extent. Matignon [1] states that ferro-boron compositions do not exhibit the same resistance to acids as in the case of ferro-silicon. Gleason [2] claims that alloys of the composition :—

Swedish iron	= 110	parts by	weight
Nickel	= 90	,,	,,
Copper	= 1	,,	,,
Aluminium	= 4	,,	,,

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are resistant to the action of nitric and sulphuric acids, and can be made without the use of deoxidizing agents. He points out also that the ordinary alloys of iron, nickel, and copper are open to the objection that the metals tend to separate throughout the mass of the alloy on cooling.

The use of nickel and chromium steel has been several times suggested for plant handling cold nitric acid. In this connection, Krupps now make a chrome steel pump for circulating acid round absorption towers for nitrous gases, but it is fairly certain that the metal used is not a simple alloy of iron and chromium, but contains a small percentage of a rare metal such as tungsten. Relative to such chromium steels, Borchers (1918), in the United States, has patented the addition of 2–5 per cent. of molybdenum to an iron-chromium alloy containing about 10 per cent. chromium and no carbon. He also states that an alloy containing 36 per cent. iron and 60 per cent. chromium is insoluble in boiling nitric acid, and can be machined as easily as iron. Titanium and vanadium have not the effect on iron-chromium alloys possessed by molybdenum.

Nickel and chromium steels containing about 10 per cent.

[1] *l.c.* [2] U.S. Pat. 1,093,557, 1914.

of nickel or chromium have a number of uses in chemical industry, even for nitric acid work. The author has used nickel steel converters for ammonia oxidation work and they have been quite successful. In this connection also a number of tests of metals and alloys available for such a piece of apparatus were carried out. All the experiments were performed at air temperature, and the test pieces completely immersed in the acid. The results (Table 21) have been calculated to show the life of a 1-inch cube of the alloy, assuming it to be attached simultaneously from two opposite sides.

TABLE 21

Alloy.	Concentration of Nitric Acid used.	Life of 1-inch Cube.
Tantiron	50%	$6{\cdot}5 \times 10^5$ days
Ironac	,,	$2{\cdot}6 \times 10^5$,,
Regulus	,,	$4{\cdot}2 \times 10^2$,,
Phosphor-bronze	,,	4 hours
Chrome steel (10% Cr)	,,	3,880 days
Nickel steel (10% Ni)	,,	1,550 ,,
Stellite	,,	608 ,,
Stellite	30%	7×10^4 days

The lead-tin-antimony alloy, regulus, although exceedingly useful for sulphuric acid, is not so useful for nitric acid work, owing to the rate of attack by nitric acid whether dilute or concentrated. Silicon-fluxed regulus metal apparatus is available, however, and is a great improvement on the ordinary regulus metal. Such type of apparatus is made by Marcus Allen & Sons, Manchester.

Several new alloys, tantcopper and tantlead, have been brought out recently by the Lennox Foundry Co. (London), for which resistance to nitric acid and other acids is claimed, but little experience seems to have been gained with them as yet in industrial operation.

Nitrosyl Sulphuric Acid

This substance, which occurs in sulphuric acid chambers where the water supply is deficient, is known as Chamber

crystals. Inasmuch as it has several uses in absorption practice, a brief description of its properties is given.

Preparation. 1. By adding nitrogen tetroxide or nitrogen trioxide to cooled concentrated sulphuric acid.[1]

$$N_2O_3 + 2H_2SO_4 \rightleftharpoons 2SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + H_2O$$

$$N_2O_4 + H_2SO_4 \rightleftharpoons SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + HNO_3.$$

2. By leading sulphur dioxide into cooled fuming nitric acid.[2]

$$SO_2 + O_2N{\cdot}OH = SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix}$$

The reaction is not so simple as this in reality, as the nitric acid is probably first reduced to nitrogen trioxide by the sulphur dioxide, which is itself oxidized to sulphuric acid; the nitrosyl sulphuric acid being the product of the secondary reaction between these two substances.

3. By leading nitrosyl chloride into concentrated sulphuric acid.[3]

$$NOCl + SO_2\begin{matrix}<^{OH}_{OH}\end{matrix} = SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + HCl.$$

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4. By the action of chlorsulphonic acid on silver nitrite.[4]

$$Cl \cdot SO_2 \cdot OH + AgNO_2 = SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + AgCl.$$

5. By the action of nitrosyl chloride on silver sulphate.[5]

$$SO_2\begin{matrix}<^{OAg}_{OH}\end{matrix} + NOCl = SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + AgCl.$$

Properties.—As prepared by these methods, the substance is obtained in colourless, crystalline plates, which melt at 73° C.[6]

The crystals readily decompose in moist air with the evolution of nitrogen trioxide,

$$2SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + H_2O = 2SO_2\begin{matrix}<^{OH}_{OH}\end{matrix} + N_2O_3.$$

[1] Weber, *Pogg. Annalen*, 1861, 341. [2] *Ibid.*
[3] Tilden, *Chem. Soc. Trans.*, 1874, **27**, 630.
[4] Thorpe, *Chem. Soc. Trans.*, 1882, **41**; 297.
[5] Berl, *Zeitsch. angew. Chem.*, 1910, **23**, 2252.
[6] Girard and Pabst, *Bull. Soc. Chim.*, 1877, **29**, 482.

With small quantities of water an intensely blue liquid is formed, the colour probably being due to the formation of nitrous acid.

Nitrosyl sulphuric acid is soluble in concentrated sulphuric acid, giving solutions which are very stable to the action of heat; the solutions can be heated to their boiling-point without appreciable decomposition. The stability of the solution in sulphuric acid decreases with increase in dilution of the sulphuric acid, and when the concentration of the latter is less than 64 per cent. H_2SO_4, the solution decomposes even in the cold. With sulphuric acid of 68·5 per cent. H_2SO_4, the whole of the dissolved nitrosyl sulphuric acid is decomposed by heating to the boiling-point of the solution.[1] In general the solution in sulphuric acid is more stable at low than at high temperatures. Lunge's results are probably explainable by reference to the hydrates of sulphuric acid. It is well known that the largest contraction in volume occurs when concentrated sulphuric acid is diluted to 73·1 per cent. H_2SO_4, which corresponds theoretically to a hydrate $H_2SO_4.2H_2O$. This hydrate exists at low temperatures, but is unstable at higher temperatures, decomposing into a lower hydrate and "free" water, which latter is effective in decomposing any nitrosyl sulphuric acid present in such a solution. The hydrate $H_2SO_4,3H_2O$ corresponds to a solution of 64·47 per cent. H_2SO_4, which is the approximate concentration of sulphuric acid in which nitrosyl sulphuric acid is decomposed at ordinary temperatures.

When nitrosyl sulphuric acid is warmed to 85° C. with dry sodium chloride, nitrosyl chloride is evolved,

$$SO_2\begin{matrix}<^{ONO}_{OH}\end{matrix} + NaCl = NOCl + SO_2\begin{matrix}<^{ONa}_{OH}\end{matrix}$$

and with sodium bromide, nitrosyl bromide is obtained.

If the acid is heated with potassium nitrate a vigorous evolution of nitrogen tetroxide occurs,

$$SO_2\begin{matrix}<^{OH}_{ONO}\end{matrix} + KNO_3 = SO_2\begin{matrix}<^{OH}_{OK}\end{matrix} + N_2O_4.$$

When treated with concentrated nitric acid, nitrosyl sul-

[1] Lunge, *Sulphuric Acid and Alkali*.

phuric acid is decomposed with the production of nitrogen tetroxide and sulphuric acid, showing that the reaction

$$N_2O_4 + SO_2\begin{matrix}OH\\OH\end{matrix} \rightleftharpoons SO_2\begin{matrix}OH\\ONO\end{matrix} + HNO_3$$

is reversible, a result which is of importance in the denitration of waste acids containing sulphuric acid and nitric acid. Nitrosyl sulphuric acid will not attack metals such as iron, aluminium, etc., unless moist, and for this reason has been suggested as a convenient form in which to transport nitrogen tetroxide or nitric acid.

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CHAPTER II

THEORETICAL PROBLEMS OF ABSORPTION

The methods used for the conversion of nitrous gases into products of commercial value are dependent on several important factors.

1. The concentration of nitrogen oxides in the gases to be dealt with.
2. The final product desired.
3. Local and economic conditions.

The arc process for nitrogen fixation requires the handling of relatively large volumes of a gas containing only 1–1·5 per cent. of nitrogen oxides. The artificial silk and celluloid industries have to deal with concentrations of 2–5 per cent. nitrogen oxides. Ammonia oxidation results in a gas containing approximately 7 per cent. of nitrogen oxides, while in processes for the denitration of waste acids from explosives manufacture, the concentrations available may be between 15–20 per cent. In each case the most advantageous process from an economic point of view is not necessarily the most advantageous from a chemical standpoint.

Although it is possible, with most commercial concentrations, to recover the bulk of the oxides as dilute nitric acid, which may be subsequently concentrated, the questions of transport and availability for commercial uses affect the various industries to a different extent. While in dyestuffs manufacture, for example, the concentrated nitric acid finally produced is readily re-absorbed into the manufacturing cycle, this is not the case with a fixation plant whose biggest market is in solid fertilizers. The question of the ultimate product to be made therefore must be decided by local needs and by the available market. The question is further discussed in Chapter VII.

The general methods of absorption of nitrous gases may be roughly classified as follows:

1. Water absorption processes.
2. Processes involving the use of alkalies, either solid or in solution, where the end product may be a pure nitrate or nitrite, or a mixture of these.
3. Absorption by concentrated sulphuric acid.
4. Absorption by certain salts.
5. Processes similar to the above (1–4), but which involve preliminary liquefaction of the nitrous gases, or alternatively processes in which the nitrous gases are concentrated before absorption.

It is proposed to consider firstly the absorption of oxides of nitrogen by water, but before discussing this type of absorption in detail, some of the general theory underlying the absorption of nitrous gases will be considered.

Chemical reactions which are caused to take place between liquids and gases need to be considered in the light of the main reaction or product it is desired to produce. In many plants a gas is washed by contact with suitable liquids, and is thereby deprived of one or more of its constituents which may be of value. The scrubbing of coal gas by water for ammonia, or by cresol for benzene, etc., is an instance in point. In this case the main object is to remove the whole of the ammonia or benzol from the gas, and the concentration of these products in the resulting solution is a secondary consideration. In other cases, such as the saturating of brine with ammonia, or the gasification of various alkaline liquids with carbon dioxide, the object in view is the complete saturation of a liquid with one of the constituents of a gas. There is finally a third type of absorption, in which it is required to absorb completely one of the constituents of a gaseous mixture, and simultaneously to saturate the liquid completely. In all these types of absorption, the simplest is that in which the process is one of simple solution, and most absorption in chemical industry is of this type.

The literature on the theory of absorption is very scanty, but the pioneer work of Hurter[1] should be mentioned. He pointed out that in general the extent of absorption will be governed by the number of molecules of gas which impinge on

[1] *J. Soc. Chem. Ind.*, 1885, 1887, 1889, 1893.

a number of molecules of the liquid absorbent in a given time. This general statement naturally takes account of such factors as temperature, pressure, velocity, etc. Hurter classified three methods of securing the necessary contact between gas and liquid:—

1. When the gas, divided into small bubbles, passes through a column of liquid.

2. When the liquid in the form of fine drops falls through a column of the gas.

3. When the gas is passed in a stream through solids with extensive surfaces which are covered by a film of liquid.

He found in general that the velocity of gas bubbles up a column of liquid was practically uniform, and drew certain general conclusions as to the relative economy of forcing gases through liquids under pressure, or drawing them through under vacuum.

The conditions in general, however, did not apply specifically to the absorption of nitrous gases.

The general question of absorption has been more recently considered by Donnan and Irvine,[1] who take account of the fact, shown by Adeney and Becher,[2] that the rate of solution of a gas in a liquid depends on the degree of unsaturation existing at the moment. Donnan and Irvine introduced the following simplifying assumptions:—

1. Temperature is kept uniform and constant throughout the tower.

2. The volume percentage of the absorbable gaseous constituent is supposed to be fairly small, so that volume changes due to its removal can be neglected.

3. The solubility of the main gaseous constituent is neglected.

4. The vapour pressure of the scrubbing liquid is supposed to be such that volume changes due to the saturation of the gas with this vapour may be neglected.

5. The flow of gas and liquid is supposed to be uniformly distributed over every cross section of the packing.

6. The wetted area of the sides of the tower is neglected in comparison with the wetted area of the packing.

[1] *J. Soc. Chem. Ind.*, 1920, **39**, 23.
[2] *Proc. Royal Dublin Soc.*, 1918–19, **15**, [*N.S.*], 385, 609.

7. The absorption is not complicated by relatively slow chemical reactions in either gas or liquid, but is a simple physical absorption.

A number of equations were obtained, for details of which the original paper should be consulted. In their present form, however, they do not apply specifically to the absorption towers for nitrous gases. This type of absorption has been specifically considered by Partington and Parker.[1] They deduced a general equation $\log_e \frac{c_0}{c} = \frac{KkA}{V} x$,

where c_0 initial concentration of entering gas in lbs. NO_2 per cubic foot.

c its concentration at a height x in the tower in lbs. NO_2 per cubic foot.

A cross section of the tower in square feet.

V rate of gas flow in cubic feet per minute.

k area of packing surface exposed in square feet. per cubic foot gross volume occupied by packing.

K a coefficient (not constant) depending on the rate of absorption of NO_2 in various concentrations of nitric acid calculated from the results of Rideal.[2]

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The equation gives approximate results for the size of towers required to carry out the absorption of a given amount of NO_2 from a gas of given concentration, by means of a solvent containing a given amount of nitric acid. The method of treatment is interesting in presenting a simplified solution of a very complicated mathematical problem. Such factors as the change in volume of the gases, change in concentration of nitric acid, rate of solution of nitric oxide in nitric acid, etc., have been neglected, but the solution is a definite step towards putting absorption practice on an exact basis.

The Absorption of Nitrous Gases by Water

This is the method almost universally adopted, and in consequence the method which involves detailed consideration,

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 75r.
[2] *J. Ind. Eng. Chem.*, Dec. 1920.

The process consists in principle in the passage of nitrous gases through a series of vertical towers, through which is being circulated a counter-current of water. The gas enters the base of the tower at one end of the series, and passing up this, is carried to the base of the next tower and so on. The water is fed in at the top of the tower at the opposite end of the series, and passing down this, is elevated to the top of the next tower and so on, becoming more concentrated in nitric acid as it goes on through the series. The two important phases are gaseous and liquid, and it is proposed to consider the theoretical factors affecting these phases before reviewing their practical application.

1. Gaseous Phase

It is generally accepted that the reactions governing the absorption of nitrous gases by water are:

(*a*) $N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2$,
(*b*) $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$,
(*c*) $2NO + O_2 \rightleftharpoons N_2O_4$.

It is evident from these reactions, therefore, that the gaseous phase will be influenced by the factors of temperature, pressure and concentration, and also, in its relation to the liquid phase, by its velocity.

Temperature. Of the three reactions previously mentioned:—

(*a*) is exothermic, but the amount of heat evolved has not been accurately determined on a thermo-chemical basis,

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2 + x \text{ cal.};$$

(*b*) is endothermic,

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \quad -18{\cdot}4 \text{ cal.};$$

(*c*) is strongly exothermic,

$$NO + O \rightarrow NO_2 + 14{,}000 \text{ cal.}$$

Consider the effect of temperature on (*a*). It is probable that only N_2O_4 molecules react with water to form nitric acid, since it can be shown that at temperatures above those at which the N_2O_4 molecule is completely dissociated into NO_2 molecules, the absorption of the gas by water is negligible, nor

is nitric acid formed in the vapour state. Since therefore a rise in temperature increases the percentage dissociation of the N_2O_4 molecules, it would inhibit, to a considerable extent, the rate of absorption of the gas by water, by lowering the partial pressure of the N_2O_4 molecules present.

Nitrogen tetroxide also obeys a general law of solubility of gases in water, in that a rise in temperature decreases its solubility. As it enters into chemical combination with water, it is not strictly comparable with an inert gas in this respect, neither does it obey Henry's law exactly, but only very approximately. The general result of increase in temperature, however, so far as the reaction (*a*) is concerned, would be to lower the rate at which N_2O_4 molecules are being extracted from the gas by the liquid absorbent.

The reaction (*b*) has been shown by Briner and Durand [1] to be endothermic, and the decomposition of nitrous acid is promoted by increase in temperature. It should be borne in mind, however, that the rate of decomposition of nitrous acid in aqueous solution is exceedingly rapid, even at ordinary temperatures, though its velocity of decomposition is promoted by rise in temperature. At 0° C. the maximum concentration obtainable is approximately 0·185 $\bar{N}$, or about 0·8 per cent. by weight. At ordinary temperatures the concentration is only 0·2 per cent. by weight. Reference to the work of Knox and Reid (Figs. 9, 10, 11) will show that the velocity of decomposition is very rapid, even at concentrations of less than 0·1 per cent. The advantage to be gained therefore by accelerating what is already a very rapid reaction is negligible.

The velocity of the reaction (*c*), viz. the oxidation of nitric oxide, has a negative temperature coefficient, i.e. it is retarded by rise in temperature. The curve plotted from the results of Bodenstein, given on page 25, shows this quite plainly, the velocity constant at 0° C. being 8·9, and at 90° C. 2·5, i.e. the velocity is reduced to one-third at the higher temperature. The oxidation of nitric oxide is the greatest "time reaction" in the absorption system, and is the main factor governing the capacity of the system. Any reduction in the velocity of the re-oxidation of nitric oxide, therefore, reacts directly and unfavourably on the capacity of the system. This will be made

[1] *Compt. rend.*, 1912, **155**, 582, 1495.

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clear when the effect of such unoxidized nitric oxide on the cycle of reactions is considered. The immediate result will be that the gas will react towards the water (with an equivalent of nitrogen tetroxide) as nitrogen trioxide, N_2O_3.

$$N_2O_3 + H_2O = 2HNO_2$$

Nitrous acid will be exclusively produced, and will then decompose according to the equation previously given, into nitric acid and nitric oxide, which latter will again "fix" its equivalent of NO_2, and dissolve as N_2O_3. It is evident that from three molecules of nitrogen trioxide we shall obtain only two molecules of nitric acid, whereas if the nitric oxide had been completely oxidized to N_2O_4, we should obtain four molecules of nitric acid from three molecules of the tetroxide, as will be obvious from an inspection of the equations representing the reaction. As a result of one complete cycle of reactions in the two cases, therefore, it is evident that the net conversion of oxides of nitrogen into nitric acid in the latter case is twice that which occurs in the former case, and consequently the absorptive capacity of the system would be halved under the former conditions. It must also be pointed out that nitric oxide will reduce nitric acid with a very appreciable velocity.

The velocity of the reaction has been determined by Saposchnikoff.[1] He showed that concentrated nitric acid is reduced very much more rapidly by nitric oxide than is dilute nitric acid, the velocities for 5 per cent. HNO_3, as compared with 65 per cent. HNO_3, being of the order of 1 : 25. An inspection of the equation for the reduction of nitric acid by nitric oxide will also show that the equilibrium is directly influenced by the partial pressure of the nitric oxide, an increase in this partial pressure favouring the reduction of nitric to nitrous acid. Those factors in absorption, therefore, of which temperature is one, which tend to cause the presence of unoxidized nitric oxide in the inlet gases, or which lower the rate of re-oxidation of the regenerated nitric oxide, require very careful control if efficient results are to be obtained.

There is finally to be considered the effect of increased temperature on the evaporation of nitric acid from the solution, caused by the passage of inert gases through the absorbent.

[1] *J. Russ. phys. Chem. Soc.*, 1901, **32**, 375.

This increases rapidly with temperature, as is well known, and consequently lowers the final concentration of nitric acid produced. To sum up, therefore, an increase in the temperature of the gases has the following theoretical disadvantages :—

1. It lowers the partial pressure and solubility of nitrogen tetroxide.
2. Lowers the velocity of oxidation of the regenerated nitric oxide.
3. Increases the amount of nitrogen trioxide in the system.
4. Decreases the capacity of the absorption system.
5. Increases the amount of evaporation of nitric acid.
6. Lowers the concentration of nitric acid which can be produced from a given concentration of nitrogen tetroxide.

These deductions have been readily confirmed by experiment and in practice. Foerster and Koch [1] obtained the following results by bubbling nitrogen tetroxide mixed with oxygen at different temperatures through absorption vessels containing water.

TABLE 22

Temperature of Gases. °C.	Concn. of HNO_3 in absorbing Solution after a given Time.
0°	54·36 per cent.
15°–18°	54·21 „ „
50°	51·84 „ „

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The figures indicate that little or no advantage is to be gained by cooling the gases below air temperature, a conclusion which is also borne out by experience in large-scale practice. So far as the diminution in rate of absorption is concerned some experiments carried out by the author showed a drop of approximately 4 per cent. in the efficiency of a tower by an increase of temperature from 25° C. to 35° C.

It is a matter of common experience in large-scale practice that an increased temperature of the gases in an absorption system (or also of the absorbing liquid) results in a lower concentration of nitric acid being obtained. For example, the

[1] *Zeitsch. angew. Chem.*, 1908, **21**, 2161.

results given in Table 23 were noted on an absorption plant consisting of eight towers in series, each 12 feet high and 3 feet 6 inches diameter, the gases being cooled to different temperatures before admission to the towers.

TABLE 23

Temperature of Gases, °C.	Percentage Concentration of Nitric Acid produced with constant Water Feed.
25°-30°	54·2 per cent.
37°-40°	53·4 ,, ,,
45°-52°	50·0 ,, ,,
55°-60°	44·6 ,, ,,

In another case a gas-inlet temperature of 70° C. caused the formation of a nitric acid containing only 30 per cent. HNO_3, while the same gas, cooled to 40° C. before admission to the tower, gave an acid containing over 45 per cent. HNO_3. In practice little or no advantage is to be gained by cooling the gases to temperatures lower than 15°–20° C., while experience shows that the temperatnre may be allowed to rise as high as 40° C. without a very appreciable falling off in the rate of absorption taking place. Above this temperature, however, the concentration of nitric acid obtainable under a given set of conditions falls off very rapidly, throwing an increasingly heavier load on the absorption system. The temperature of 40° C. should therefore be regarded as a maximum, though it is eminently desirable that the gases should be cooled down to air temperature if possible. The amount of published experimental data with regard to this temperature limit is negligible, and the figure of 40° C. is derived mainly from experience. In this connection it is interesting to notice that Taylor, Capps, and Coolidge [1] state that a temperature of 40° C. is considered to be a maximum for the inlet gases in American absorption practice.

Cooling of Nitrous Gases. It is possible in most cases to keep the temperature of the gases below the maximum of 40° C. in winter, particularly in plants where the initial tem-

[1] *J. Ind. Eng. Chem.*, 1918, **10**, 270.

perature of the nitrous gases is relatively low, or the gases are small in quantity. Such types include, for example, the denitration of waste acids, nitric acid manufacture by the pot process, the artificial silk industry, etc. Even in summer there is no great difficulty with the gases from these plants.

The reverse is the case however with the gases obtained by the oxidation of ammonia, where the gases leave the converter at temperatures in the region of 600° C., and above all in the arc fixation process, where temperatures of over 1,000° C. may occur in the gas leaving the furnace. In such cases cooling is quite essential. As is well known, the gases from the arc furnaces are deprived of a good deal of their heat under boilers, the issuing temperature being around 150°–200° C. to avoid corrosion of the boiler plates by the deposition of weak nitric acid. After this they are led through long air-cooled and water-cooled mains, so that they are very nearly at air temperature before reaching the absorption towers. At Notodden, for example, this is effected by carrying the gases through aluminium mains 5 feet diameter and over 1,200 yards long.

In ammonia oxidation plants, as previously stated, the gas comes away from the converter at a temperature of approximately 600° C. In this case the gases are partly air-cooled, and then passed through a cooler, built of acid-proof brick and containing internally water-cooled pipes of acid-resisting iron.

With almost any absorption plant, however, it is advisable, and in fact necessary, to provide some simple means of cooling the gases before allowing them to enter the absorption towers. In most plants the gas initially to be dealt with consists of nitric oxide, which must be oxidized to the tetroxide before the gas enters the towers. Since the reaction between nitric oxide and oxygen is exothermic, a sharp rise in temperature of the gases occurs, on adding the air necessary for the oxidation. An approximate idea of the temperatures likely to be attained where large concentrations of nitric oxide have to be handled may readily be obtained from the data of Thomsen and Berthelot, on the heats of formation of the oxides of nitrogen.

1. $N + O \rightarrow NO$ — 21,600 cals.
2. (at 22° C.) $N + O_2 \rightarrow NO_2$ — 1,700 cals.
3. (at 150° C.) $N + O_2 \rightarrow NO_2$ — 7,600 cals.

Subtracting (1) from (3) we obtain the heat of formation of NO_2 at 150° C. (the temperature at which N_2O_4 mols. are completely dissociated into NO_2 mols.).

$$NO + O = NO_2 + 14{,}000 \text{ cals.}$$

Consider the addition of the theoretical amount of oxygen (as air) to a quantity of pure nitric oxide. 22·4 litres (30 grams) NO will form 22·4 litres (46 grams) of NO_2, assuming complete dissociation, and will require for oxidation 11·2 litres of oxygen, which will be associated with 44·8 litres (56 grams) of nitrogen. Since the specific heat of nitrogen tetroxide (as NO_2) is 1·65 cals. per gram, and of nitrogen 0·23 cals. per gram, we have

$$(R \times 46 \times 1{\cdot}65) + (56 \times 0{\cdot}23 \times R) = 14{,}000 \text{ cals.}$$

where R = rise in temperature in deg. Cent.

whence R = 160 deg. Cent. (approx.).

Hence if the initial temperature of the gases was 18° C., we should obtain theoretically a final temperature of nearly 180° C. under the above conditions for 30 grams of nitric oxide. In practice pure nitric oxide has seldom to be dealt with, but is accompanied by varying quantities of air or nitrogen, water vapour, nitric acid, etc. The presence of these substances causes much lower temperatures to be obtained than the theoretical figure previously derived. The author has noticed repeatedly, however, that nitric oxide from a denitration plant, when previously cooled to a temperature of 18°–25° C., attained temperatures of 50°–70° C. when the theoretical amount of oxygen (as air) was added, for the oxidation of the nitric oxide to the tetroxide, and if the plant is such that radiation losses are small, it is quite possible to obtain higher temperatures than these.

The form of cooler to be adopted under such circumstances naturally depends on the quantity of gas being handled, and on its temperature. For very small quantities of dilute gases, the external water-cooling of a length of stoneware main will be found to be sufficient, although the method is liable to give trouble in practice, owing to the cracking of pipes through sudden changes in temperature, leaky horizontal joints, etc.

Hart's condensers (Fig. 34), such as are used on many nitric acid plants, have been used with considerable success

for handling gases from denitration towers, and are preferable from every point of view to the old water-cooled silica coil.

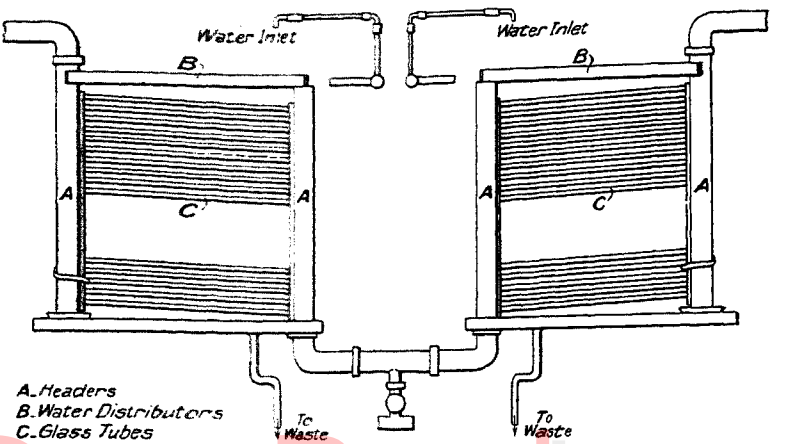

FIG. 34.—Hart's Condensers adapted as Coolers for Nitrous Gases.

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The question of cooling in the arc process has been solved by the elaborate methods previously mentioned, although such an extensive equipment for this purpose could not be entertained in most other types of plant.

Particular difficulty seems to have been experienced up to the present in ammonia oxidation systems, where a considerable quantity of water vapour is also present in the nitrous gases, and on cooling the gas to temperatures near 100° C., a weak nitric acid is deposited which is exceedingly corrosive in action. Various suggestions have been made for eliminating this water vapour, such as centrifuging, sudden cooling, etc., but none appears to be satisfactory.

The question of cooling the gases as they pass through each tower of the series in the absorption system has also met with consideration. For example, Eng. Pat. 121,635, 1919, describes a counter-current absorption system, in which refrigeration to 0° C. takes place at the water-inlet tower, and progressive reduction in temperature to the concentrated acid tower where the heat of reaction is the greatest. The advantages claimed for the process are :–

(*a*) That absorption is facilitated.

(*b*) That the speed of production is increased.

(*c*) That the process is very useful for high concentrations of nitrous gases.

On the other hand, a private communication to the author on American absorption practice states that improved results have been obtained on an absorption system by warming the last tower (water inlet) of the series, a small rise in temperature appearing to favour the more complete scrubbing of a weak gas. There appears to be no appreciable rise of temperature caused by the cycle of reactions in the ordinary water absorption system, where cooling by radiation is allowed to take place. This is undoubtedly due to the fact that any nitric oxide regenerated in the system is allowed to oxidize in the presence of wetted surfaces, and consequently little more than 50 per cent. oxidation is obtained, before the gas is reabsorbed as nitrogen trioxide to form nitrous acid.

The solution of nitrogen trioxide in water is also an endothermic reaction

$$N_2O_3\,(aq.) = -6{,}820 \text{ cal.}$$

Finally, the decomposition of nitrous acid is also endothermic, and these two changes tend to neutralize the effect of the heat evolved by the oxidation of the nitric oxide in the system, and, combined with the cooling effect of radiation, liquid circulation, etc., prevent any appreciable rise in temperature taking place.

Pressure of the Gaseous Phase

The term "pressure," in its application to the absorption system, includes both the partial pressure or concentration of the nitrogen tetroxide, and also the total pressure on the system. The partial pressure of the nitrogen tetroxide is a factor of very great importance.

Partial Pressure of Nitrogen Tetroxide. In general, the greater the solubility of a gas in water, the less will be the importance of concentration in its absorption from an industrial standpoint. With gases which are only moderately soluble, however, the partial pressure of the gas in contact with the water, being the main factor governing the rate of solution and total solubility of the gas, becomes a factor of first import-

ance, as it governs directly the capacity of the absorption system. Where the gas enters into a chemical reaction with water the importance of partial pressure is even greater, and this is particularly the case with nitrogen tetroxide since its rate of absorption depends upon the rapid establishment of certain equilibria, and also the concentration of nitric acid resulting from its absorption in water must be as high as possible. It is obvious therefore that the partial pressure of the nitrogen tetroxide will have a direct relation to the total capacity of the system. The total effect on the system is the resultant of a number of smaller effects, the most important of which are as follows:—

1. The rate of dissolution of the tetroxide in water is lowered.

This factor affects the absorption system in two ways. Firstly in decreasing the total capacity of the system in direct ratio to the decrease in concentration, and secondly in lowering the final concentration of nitric acid which can be attained. It may not at first be evident why this latter variation should occur. It has been shown by Foerster and Koch,[1] however, that the rate of solution of nitrogen tetroxide in nitric acid decreases rapidly with increase in the concentration of nitric acid in the aqueous absorbent (see Fig. 38, p. 133). The reaction between nitrogen tetroxide and water may be represented as follows:—

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2. \quad . \quad . \quad . \quad (a)$$

The nitrous acid in the solution then enters into the equilibrium reaction

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O. \quad . \quad . \quad . \quad (b)$$

It is evident from an inspection of these two reactions that the final concentration of nitric acid obtained will depend upon the velocity with which these equilibria are established, and hence, in the case of (*a*) above, on the partial pressure of the nitrogen tetroxide. The equilibrium (*b*) is established very rapidly (see Chapter I, Nitrous Acid).

2. The second effect of a low partial pressure of nitric tetroxide may be said to be rather an indirect one, but is yet of considerable practical importance, viz. the evaporative effect of large volumes of inert gas passing through fairly con-

[1] *Zeitsch. angew. Chem.*, 1908, **21**, 2161.

centrated solutions of nitric acid. This evaporative effect will be relatively larger as the partial pressure of the nitrogen tetroxide is smaller. If a certain number of tons of nitric acid per week are to be recovered in an absorption system of a given capacity, it is evident that the amount of evaporation taking place is much greater if the oxides of nitrogen form 1 per cent. of the gas mixture as compared with 10 per cent. of the mixture. Although it might be anticipated that as nitric acid forms a minimum vapour pressure mixture at 68·5 per cent. HNO_3, the evaporative effect of the inert gases would remove water rather than nitric acid, and so concentrate the acid to some extent, this is not found to be so in practice. The inert gas appears to remove nitric acid in the form of a fine mist which is very difficult to condense except by electrical precipitation. It may contain up to 40 per cent. HNO_3, and the removal of such "mist" from the system by inert gases is a fruitful source of loss, and constitutes a strong argument for the use of the highest partial pressure of nitrogen tetroxide obtainable under the given set of conditions.

3. The final effect of a low partial pressure of nitrogen tetroxide lies in the fact that the equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2$$

is displaced to the right by decrease in the partial pressure of the N_2O_4. If it be assumed therefore that only N_2O_4 molecules react with water and not the NO_2 molecule (an assumption which appears to be justified by the fact that above 140° C., the temperature at which only NO_2 molecules are present, nitric acid is not formed by admixture with steam), then the rate of dissolution of the tetroxide is further lowered, with an increased effect upon the capacity of the system, and the concentration of nitric acid, as outlined under (1) above.

The experimental work of Foerster and Koch [1] on the maximum concentration of nitric acid which is obtainable by leading mixtures of nitrous gases and air at constant velocity into water at 15° C., shows clearly the effect of partial pressure on the concentration of nitric acid produced (Table 24).

With the 7–8 per cent. NO_2-air mixtures obtained from ammonia oxidation plants, nitric acids of 58–60 per cent.

[1] *l.c.*

TABLE 24

Concentration of Nitrogen Tetroxide (per cent. NO_2 by vol.)	Concentration of Nitric Acid produced. Per cent. HNO_3
1	46
2	52
5	55

HNO_3 can be obtained, while with mixtures containing 15 per cent. of nitrogen tetroxide (as NO_2) a maximum concentration of 68 per cent. HNO_3 can readily be produced.

How important the factor of partial pressure is on the capacity of the absorption system is clearly illustrated by the gross cubic capacity of the different systems dealing with nitrous gases of widely differing concentrations. For example, the gross absorption capacity required to produce one ton of nitric acid (as 100 per cent.) per week is about 1,000 cubic feet in the case of a gas containing 1 per cent. of nitrogen tetroxide (as NO_2) such as is obtained in the arc process, while only 25–30 cubic feet are required for a gas containing about 15 per cent. nitrogen tetroxide (as NO_2) coming from the ordinary waste acid denitration plant.

Variation of the Partial Pressure of Nitrogen Tetroxide. It will be evident from what has been said that it is of the greatest economic importance in absorption practice to maintain the partial pressure of the nitrogen tetroxide as high as possible.

In many processes in which oxides of nitrogen have to be absorbed, little or no variation in the partial pressure can usually be made directly, owing to the conditions under which the gas is produced. For example, in the arc process and in ammonia oxidation the concentration of nitric oxide in the final gases is already fixed by the conditions of the oxidation.

If, on the other hand, a concentrated nitric oxide is available, as is usually the case in denitration processes and a number of oxidation processes with nitric acid, the amount of air or oxygen to be added to the nitric oxide is of direct importance in determining the partial pressure of the resulting nitrogen

tetroxide. The partial pressure of the nitrogen tetroxide can be increased with both types of gases by intermediate extraction processes such as liquefaction, absorption in weak bases and subsequent release by heating, etc. This phase of the problem has assumed such an importance, however, that it is discussed in detail later in the chapter, and it is proposed to deal for the moment with gases already rich in nitric oxide to which air or oxygen must be added to oxidize the nitric oxide to the tetroxide before sending the gases to the absorption towers. The air or oxygen added has two important functions :—

1. To oxidize all the nitric oxide originally present.

2. To oxidize the nitric oxide continuously regenerated throughout the cycle by the decomposition of nitrous acid.

The quantity of air or oxygen required for (1) above can readily be calculated, and also the theoretical quantity required for (2). It must be borne in mind, however, that any excess of air over that required for (1) has two important effects on the cycle :—

(*a*) It lowers the partial pressure of the nitrogen tetroxide entering the system.

(*b*) It increases the time required for the oxidation of the nitric oxide originally present (see Chapter I, pp. 20–24).

The results of (*a*) above have already been discussed. So far as (*b*) is concerned it is evident that the effect of dilution with oxygen is similar to that of excessive inlet temperatures in this respect. Only that proportion of nitrogen tetroxide above that required for the formation of the trioxide ($NO + NO_2$) will form nitric acid directly, and it is quite essential therefore to have such conditions as will ensure all the combined nitrogen in the inlet gas to the system being present as the tetroxide. The point has already been mentioned in discussing the influence of temperature (p. 97), where it was shown that the load on the absorption system is about twice as great for a gas containing N_2O_3 molecules as compared with N_2O_4 molecules. In addition to this fact, which is the direct result of the chemical reactions involved, it must also be taken into account that nitrogen trioxide dissolves in water at a much slower rate than the tetroxide, and also that concentrated nitric acid is readily reduced by nitric oxide.

In practice it is found that an excessive temperature in the inlet gases causes far more inefficient results than the mere presence of nitric oxide in the inlet gas if the latter is at ordinary temperature.

The following sets of observations on a set of towers attached to an absorption system will serve to illustrate the effect of excess of nitric oxide in the inlet gases, so far as the variation in the concentration of nitric acid is concerned, and particularly the reduction of concentrated nitric acid by the nitric oxide in the inlet gas.

TABLE 25

Inlet gas containing no free oxygen: N_2O_3 = 14·5 per cent.

Rate of Water Feed.	Number of Tower.	Per cent. HNO_3 in Acid at Base of Tower.
10 gals. per hour .	1 (water inlet)	48·8
	2	51·8
	3	55·2
	4	56·9
	5	57·4
	6	55·0
	7	48·7
	8 (gas inlet)	42·2

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The most concentrated acid should be obtained from tower No. 8, but is, in fact, obtained from No. 5, so that the relatively strong acid from this tower is undergoing progressive reduction as it approaches the gas-inlet tower, owing to the relatively high concentration of nitric oxide entering the system.

On admitting air so that there was an excess of 1·5 per cent. free oxygen in the inlet gases, the amount of nitric oxide in the inlet gases was reduced to 3 per cent. when the tower system operated as shown in Table 26.

The acids running away from each tower had lost the bluish-green colour possessed by the absorber acid in the previous case (Table 25), and were consistently yellow. The most concentrated acid is now obtained from tower No. 6. Air was admitted further until the inlet gas showed a 6 per cent. excess

TABLE 26

Water Feed.	Number of Tower.	Per cent. HNO_3 in Acid at Base of Tower.
10 gals. per hour .	1 (water inlet)	28·9
	2	47·0
	3	57·5
	4	60·8
	5	64·2
	6	64·8
	7	62·2
	8 (gas inlet)	56·9

of oxygen and the nitric oxide was below 1 per cent. The feed of water could then be doubled, and the results obtained are shown in Table 27.

TABLE 27

Water Feed.	Number of Tower.	Per cent. HNO_3 in Acid at Base of Tower.
20·5 gals. per hour .	1 (water inlet)	21·7
	2	35·6
	3	42·1
	4	46·0
	5	52·0
	6	52·8
	7	55·8
	8 (gas inlet)	57·5

The presence of nitric oxide in the inlet gases hence causes considerable loss in efficiency in the tower system. Care must therefore be taken that sufficient time is allowed after the addition of oxygen (as air) for the complete oxidation of the nitric oxide to the tetroxide. As will be seen from the curves on pages 20–24 the time of oxidation varies considerably with the concentration of nitric oxide in the gas mixture. For example, a mixture containing initially 20 per cent. of nitric oxide requires 19 seconds for 90 per cent. oxidation, whereas

a mixture containing initially 1 per cent. NO requires 204 seconds for a similar amount of oxidation.

This time for oxidation can only be allowed by provision of oxidation chambers, wide pipe runs, or unwetted towers, before the oxidation system.

The net oxidation capacity required can readily be calculated from the volume composition of the gases being dealt with, and their velocity. In this connection it must be emphasized that the use of wide gas mains is often more economical than the construction of special oxidation towers, needing concrete foundations, brick pier supports, drainage facilities, etc.

Moscicki [1] describes an absorption system in which the absorption vessel alternates with an oxidation vessel (see p. 174). A similar device is patented [2] by which it is proposed to lead away the gases after each tower and allow the nitric oxide to oxidize completely to nitrogen tetroxide before leading the gas to the next tower in the series.

It must be pointed out, however, that the concentration of nitric oxide in the gases becomes rapidly less as the gas passes through the system. The gas would therefore need to be given an increasingly longer time of passage between each pair of towers to secure complete oxidation to nitrogen tetroxide each time. Although the size of the actual absorption vessel might be considerably diminished by so doing, the capacity of the system would not necessarily be increased, owing to the time required for the oxidation in each case, which limits the rate of flow of the gases through the system. This was actually experienced by setting up in an absorption system an alternation of packed wetted towers and unpacked dry towers.

The present system is a compromise, inasmuch as the nitric oxide regenerated is allowed to oxidize as far as N_2O_3, or even a little higher, a reaction which is relatively rapid. The nitrous acid formed by its solution in water also decomposes rapidly, one-third of its nitrogen only being converted to nitric acid. A given concentration of nitric acid is more rapidly attained by this latter cycle in the "weaker" towers of the series than if the nitric oxide had been led away and allowed time to oxidize completely to N_2O_4 before absorption in water.

[1] *Chim. et Ind.*, 1919, **11–12**, Dec. [2] Fr. Pat. 469,649, 1914.

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The alternation of oxidation chambers with absorption vessels will decrease the size of absorption tower necessary, therefore, but not necessarily the capacity of the system.

These arguments do not apply, however, to the gas entering the system, since the greatest efficiency is obviously obtained by having only N_2O_4 molecules present. The reducing action of any entering nitric oxide on the relatively strong nitric acid in the gas-inlet tower would also be much greater than with the more dilute acids in the towers near the water inlet.

The preceding discussion will make it clear therefore that where a concentrated nitric oxide is available, the amount of oxygen to be added before admission of the nitrous gas to the absorption towers is very important. In this connection it is a matter of experience that the theoretical maximum concentration of nitric acid obtainable by the absorption of nitrous gases in water (68·5 per cent. HNO_3, see p. 53) is not attainable with nitrous gases containing less than 8–10 per cent. NO, and if the concentration of nitric oxide available is greater than this figure, it should not be reduced much below it by the addition of air or oxygen. Before discussing this point in any further detail, it is necessary to determine the theoretical quantity of air necessary for the oxidation and absorption of a given concentration of nitric oxide.

Theoretical Quantity of Oxygen required. A consideration of the three main absorption reactions will show that the gas passing through the tower system is converted into a series of gas mixtures containing smaller and smaller concentrations of nitric oxide, the time of oxidation of each mixture increasing very rapidly. From the three equations referred to it is evident that six molecules of NO_2 are converted into four molecules of nitric acid and two molecules (i.e. $\frac{1}{3}$) of nitric oxide. This nitric oxide is re-oxidized, and again $\frac{2}{3}$ of the NO_2 formed is converted into nitric acid and $\frac{1}{3}$ forms nitric oxide, and so on.

Thus if N is the weight of nitrogen tetroxide (as NO_2) entering the absorbers, the amount of contact between nitrogen tetroxide and water is represented by the sum of

$$\begin{aligned} &N + \tfrac{1}{3}N + \tfrac{1}{9}N + \text{etc.} \\ &= 1{\cdot}5\ N. \end{aligned}$$

By making the assumption that the rate of formation of nitric oxide approximates to its rate of re-oxidation (which is true only for fairly concentrated nitrous gases in contact with water), the maximum weight of nitric oxide formed in any one tower [1]

$$\text{Wt. NO} = \text{N} \times 1{\cdot}5 \times \frac{2 \times 30}{6 \times 46} = 0{\cdot}326\text{N}$$

where N = weight of total nitrogen (calculated as NO_2) absorbed in each tower.

If volume changes, instead of weights of products, are considered, it is evident that 3 vols. of NO_2 will generate 1 vol. of NO, and in consequence the volume of nitric oxide generated throughout the system from 1 vol. of NO_2 will be the sum of the series

$$\Sigma = \tfrac{1}{3} + \tfrac{1}{9} + \tfrac{1}{27}, \text{ etc.}$$
$$= 0{\cdot}5 \text{ vols. NO.}$$

This result indicates therefore that the total amount of nitric oxide regenerated during the absorption cycle is one-half the amount of nitrogen tetroxide (as NO_2) entering (and absorbed) in the system. From this relationship the theoretical amount of oxygen required to accompany the nitrogen tetroxide entering an absorption system can readily be calculated.

This figure is useful in giving an approximate idea of the amount of nitric oxide developed in each tower, if the amount of nitric acid (i.e. the NO_2 absorbed) in the tower is known.

By making certain simplifying assumptions, a much clearer idea of the nature of the problem, and the influence of the initial concentration of nitric oxide and oxygen, can be obtained by calculation.

Assuming that all the nitrogen tetroxide entering a tower is absorbed, and regenerates its equivalent of nitric oxide, imagine a gas of initial composition

$$NO_2 = 15\% \text{ by vol.}$$
$$O_2 = 10\% \text{ by vol.}$$
$$N_2 = 75\% \text{ by vol.}$$

Consider 100 vols. of such a mixture. After the first tower

[1] *Tech. Records Expl. Supply*, No. I, 1915–18.

A the NO_2 will have been replaced by $\frac{1}{3} \times 15$ vols. of NO, i.e. 5 vols. NO.

The composition of the exit gas will then be

NO	= 5 vols.		NO = 5·55%
O_2	= 10 vols.	i.e.	O_2 = 11·11%
N_2	= 75 vols.		N_2 = 83·33%.

The nitric oxide is then oxidized, the 5 vols. above requiring 2·5 vols. O_2. The NO_2 is absorbed, regenerating $\frac{1}{3} \times 5$ vols. of NO. Hence composition of gas after leaving tower B is

NO	= 1·67 vols.	=	2·0%
O_2	= 7·5 vols.	=	9·0%
N_2	= 75 vols.	=	89·0%.

After tower C

NO	= 0·56 vols.	=	0·71%
O	= 6·66 vols.	=	8·10%
N_2	= 75·00 vols.	=	91·2 %.

The times of oxidation for these mixtures (see Fig. 2, p. 20) are as follows:—

TABLE 28

After Tower.	Composition of Gas (per cent. NO).	Time of Oxidation of 90 per cent. of the NO.
A	5·55%	42 secs.
B	2·0%	190 secs.
C	0·71%	1,426 secs.

The time the gases are in the absorption system varies with the type of plant, but if the longest period allowed in most large-scale plants, viz. 20 minutes, is taken as an example, it is seen that it is quite insufficient for the oxidation of 90 per cent. of the nitric oxide in the mixture after tower C. Part of this unoxidized nitric oxide will represent loss in the absorption system, unless a final absorption by alkaline solutions is carried out, when nearly all the NO present will be removed (with an equivalent of NO_2) as N_2O_3, without the regeneration of nitric oxide.

The figures given therefore serve to illustrate that the excess of oxygen allowed to be present in the inlet gas to the system must be as small as possible. The theoretical value is readily obtained from the fact that the amount of nitric oxide regenerated is 0·5 N by vol. where N = total vol. NO_2 absorbed, or 0·326 N by weight where N = total weight NO_2 absorbed. If therefore the inlet gas contains 10 per cent. NO_2 by volume, 100 vols. of the gas will give rise to a *total* of 5 vols. NO which will require 2·5 vols. of oxygen for its oxidation. For every 100 vols. of original gas, therefore, there should be added theoretically 2·5 vols. of oxygen. If we assume the 100 vols. contain $\left.\begin{matrix}90 \text{ vols. } N_2\\ 10 \text{ vols. } NO_2\end{matrix}\right\}$, and that the 2·5 vols. oxygen is added as air, the gas will then contain

100 vols. N_2
10 vols. NO_2
2·5 vols. O_2

and its percentage composition would be

N_2 = 88·89%
NO_2 = 8·89%
O_2 = 2·22%.

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The curve (Fig. 35) is obtained by calculating the values thus obtained for a series of initial percentages of nitrogen tetroxide in the inlet gases, and shows the theoretical amount of oxygen required for any given percentage of nitrogen tetroxide in the inlet gases. This quantity of oxygen is the minimum necessary, if all the regenerated nitric oxide is to be oxidized completely to the tetroxide. It must be remembered in practice however that the complete oxidation of nitric oxide seldom occurs, since the reaction takes place in the presence of moisture, which absorbs nitrogen trioxide, or its equivalent of nitric oxide and tetroxide, as fast as it is formed. The nitrogen trioxide subsequently regenerates nitric oxide through the intervention of nitrous acid. It can readily be seen that in such a cycle of reactions the quantity of oxygen required for the production of a given amount of nitric acid would be the same in the two cases.

Method of Addition of Oxygen. In practice the air from the acid elevators (Pohle lifts, etc.) is usually admitted to the

towers, and a certain amount of air also enters by leakage through acid taps, jointing, etc.

Let us consider a system of eight small towers giving 400 lb. of 50 per cent. HNO_3 per hour. The water circulated is at least 20 gallons per hour, and this is being circulated in each of eight towers. If we take as an approximation that a Pohle

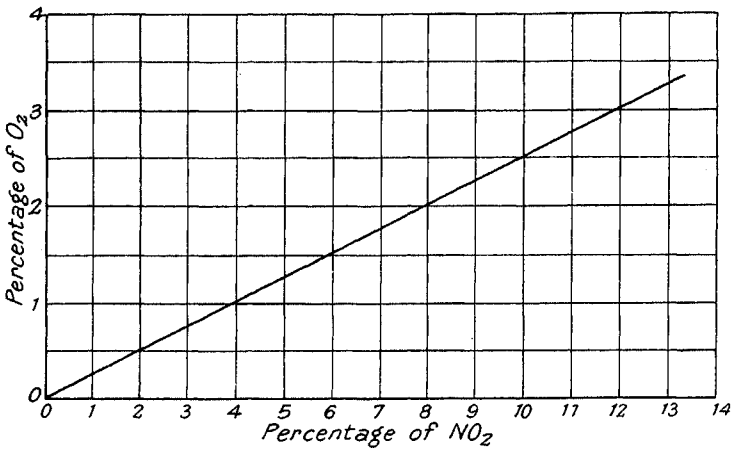

FIG. 35.—Curve showing Theoretical Quantity of Oxygen required for a given Percentage of Nitrogen Tetroxide in the Inlet Gases to an Absorption System.

lift uses about six volumes of air to elevate one volume of acid, we have, entering the system per hour,

$$\frac{8 \times 6 \times 20}{6{\cdot}25} \text{ cubic feet of air}$$

$$= \text{approx. } 160 \text{ cubic feet air}$$
$$= 40 \text{ cubic feet oxygen.}$$

The amount of nitrogen tetroxide entering per hour corresponds to 200 lb. HNO_3 (as 100 per cent.), which is formed from 146 lb. of NO_2

$$= 1{,}114 \text{ cubic feet } NO_2.$$

This would regenerate by complete absorption a total amount of nitric oxide in the system equal to 557 cubic feet, which would require for oxidation 278·5 cubic feet of oxygen. Thus the sole addition of air from the Pohle lifts is quite inade-

quate for the absorption unless a considerable excess of liquid absorbent is kept in circulation in each tower. It is therefore necessary to supplement the air added to the gases from the air lifts. This is usually carried out by injecting compressed air into the nitrous gases before the oxidation chamber is reached, or else by using the velocity of the nitrous gases themselves as a means of sucking in the necessary air supply. It is at this stage of the absorption system that a totally inadequate control is commonly observed in most absorption plants. The usual type of error in operation is probably one of the following:—

1. The injection or "induction" of air without any attempt to check its quantitative relationship with the amount of nitric oxide present.

2. The air is admitted at a point which allows insufficient time of oxidation before the gas is admitted to the towers.

3. The air from the Pohle lifts is injected into the nitrous gases immediately before entering the tower system, so that the effect of the added oxygen is comparatively small.

4. The system being worked under suction, a considerable amount of air leakage is allowed to take place.

DIGIBOOKS

So far as (1) above is concerned, it is hoped that the need of such measurements will have been made quite evident. With the factor of time of oxidation is also involved the temperature rise on adding air or oxygen to nitric oxide, so that it is also self-evident that the air should be injected before the coolers. The third point above, which is a very common fault in most absorption systems, can readily be overcome by leading this air (containing nitrous gases) into the tower containing gases most closely approximating to its composition. This will usually be found to be the third tower from the gas inlet. The amount of air leakage on most plants is very excessive. It can be almost entirely eliminated by attention to pipe-joints, etc., and particularly to the luting of the acid-outlet taps from the towers. A common cause of leakage near the water-inlet towers (to which end of the system the fan is usually attached) results from the use of a very dense packing necessitating a considerable suction on the towers.

On the whole, the most convenient method of adding air to the nitrous gases is to blow it into the main through a standard

jet which can readily be calibrated for different air pressures. The quantity of air can then be rapidly adjusted to suit the nitric oxide content of the gases, without the necessity for a large number of gas analyses.

It has also been found experimentally that an apparently convenient method of controlling the working of the towers is by the amount of oxygen in the *exit* gas from the system.[1]

They found that the oxygen content of the exit gas should not be allowed to fall below 4 per cent. O_2, between 5–6 per cent. O_2 corresponding with the highest absorption efficiency. The method has not yet been tried very extensively on a large scale, but offers a very convenient method of control, in spite of the extra care needed to prevent air leakage into the system.

The figures given for the nitric oxide content of the gas after successive towers (A, B, C . . ., p. 113) serve also to emphasize the fact that since the gas is becoming increasingly dilute with respect to NO, with consequent increase in its time of oxidation, this gas will tend to form the main oxide of nitrogen in the gas towards the end (water inlet) of the absorption system. Since this nitric oxide will be associated with an equivalent amount of nitrogen tetroxide (the oxidation of 50 per cent. of the NO in any mixture with air being comparatively rapid), it is evident that the nitric acid obtained in the towers near the end of the series is formed almost exclusively by the decomposition of nitrous acid, and that loss of nitric oxide to the exit is inevitable if water is the absorbent. Nitrogen trioxide is also more slowly absorbed by water than nitrogen tetroxide. On the other hand, N_2O_3 is absorbed more rapidly by alkalies and sulphuric acid than is N_2O_4. The use of an alkaline absorbent at the end of an absorption system, therefore, gives a much more efficient absorption. The less the concentration of nitrogen tetroxide in the inlet gases to the absorption system, the greater the need for such alkaline absorbents at the end of the system. In the Norwegian Hydro-electric Company's works at Rjuken, where only very low concentrations of nitrous gases are available, about 15 per cent. of the total fixed nitrogen is recovered as pure nitrite in this way. With more concentrated nitrous gases, the proportion of nitrite is much less than this, and in ammonia oxidation

[1] Taylor, Capps and Coolidge, *J. Ind. Eng. Chem.*, 1918, **10**, 270.

practice, for example, does not amount to more than 4–5 per cent. of the total fixed nitrogen.

To sum up, therefore, it is evident that the maintenance of the highest possible partial pressure of nitrogen tetroxide is of fundamental importance inasmuch as it is directly related to the total capacity of the absorption plant, and to the market value of the nitric acid produced. Some of the errors in operating absorption plants which cause low partial pressures to be obtained have already been mentioned. As was stated at the beginning of the discussion on this subject, the concentration of nitrogen tetroxide is already fixed on some types of plant, and no direct variation is possible. The suggestions previously outlined apply mainly to nitrous gases of fairly high concentration. Before dealing with methods of securing high concentrations which involve intermediate liquefaction or absorption, it must be pointed out that there are certain obvious methods of maintaining high concentrations of nitrogen tetroxide which are uneconomical at the present time, and are only of theoretical interest. Such a device, for example, is the addition of oxygen or ozone instead of air to nitric oxide. The use of oxygen might be possible if a very cheap source could be obtained, but at present the cost is prohibitive.

BiggBooks

There are a number of patents designed to secure the maintenance of a high partial pressure of nitrogen tetroxide by suitable modifications in the absorption system, some of which are of interest. One of these [1] describes a system in which absorption vessels of relatively small capacity are made to alternate with large oxidation chambers so that the gases pass through each in succession. As pointed out previously, the idea underlying this device is somewhat fallacious, and the capacity of the system is not increased.

Another patent [2] proposes that the gas be subjected alternately to three types of treatment:—

(*a*) Absorption of $\frac{2}{3}$ of the combined nitrogen ($\frac{1}{3}$ forms nitric oxide).

(*b*) Desiccation of the residual gas by treatment with anhydrous calcium nitrate, or other drying agent.

(*c*) Oxidation of the nitric oxide to nitrogen tetroxide.

[1] Fr. Pat. 469,649, 1914; cf. Fr. Pat. 385,605, 1907.
[2] Fr. Pat. 385,569, 1907.

Concentration of Nitrous Gases as a means of obtaining a high partial Pressure of Nitrogen Oxides. The advantages of a high concentration of nitrogen tetroxide are so important that a considerable number of methods have been devised to concentrate the nitrous gases before absorption. When it is considered that 1,000 cubic feet gross tower space is required to make 1 ton of nitric acid per week from a gas containing 1 per cent. NO_2, while only 25–30 cubic feet are required to make a similar amount of acid from a gas containing 10–15 per cent. NO_2 in the same time, it is evident that a very considerable capital expenditure in tower construction may be saved by using some intermediate concentration process. It must be emphasized, however, that the experience gained of such intermediate concentration processes in this country is almost negligible, and so far as can be judged from the tendencies of the larger fixation plants, the cost of such intermediate concentration is such as to favour the direct absorption of dilute nitrous gases by alkaline absorbents with the production of nitrites and nitrates.

The processes for concentration which have been put forward may be conveniently divided into two classes :—

(*a*) Absorption in solids or inert liquids and subsequent release by heat, or other treatment *in situ*.

(*b*) Liquefaction.

The Allgemeine Elektrochemisches Gesellschaft [1] describes the absorption by oxides of zinc, copper, or lead. The salts so formed are then decomposed by heating in iron retorts to 500° C. (or *in vacuo* to 200°–300° C.), when pure nitrogen tetroxide is evolved. The same firm [2] also subject a mixture of nitric oxide and nitrogen tetroxide and air to powerful centrifugal action at low temperatures, when a mist of nitrogen tetroxide separates. Ramsay [3] describes the use of salts which are capable of entering into a reversible reaction with nitric acid, e.g. phosphates. The action of the oxides of nitrogen is continued until all the nitrite is converted into nitrate. The temperature is then raised, steam is blown in, and nitric acid distils over. Another patent [4] recommends the absorption of oxides of nitrogen by solid, dry absorbents, e.g. phosphates,

[1] Eng. Pat. 8,426, 1908.
[2] Eng. Pat. 9,233, 1908.
[3] Eng. Pat. 16,067, 1907.
[4] Eng. Pat. 16,068, 1907.

and oxides of magnesium, aluminium, and iron. When heated to 300° C., the salts yield oxides of nitrogen in a concentrated form. Eyde.[1] concentrates nitrous gases by absorption as nitrites, and subsequent liberation by dilute nitric acid.

The well-known property of solutions of ferrous, cobaltous, and nickelous salts of absorbing nitric oxide, which is subsequently released by heat, is also used for concentrating oxides of nitrogen : e.g. Delplace [2] absorbs the gas in ferrous sulphate solution, and then recovers it by heating. Guye [3] describes the use of solvents such as chloroform, carbon tetrachloride, ethyl chloride and bromide, for the extraction of nitrogen tetroxide from gaseous mixtures with air. Amyl acetate, for example, absorbs 20 per cent. of its weight of oxides of nitrogen which can be obtained as nitric acid by the addition of water. A similar patent to that of Ramsay (*l.c.*) [4] describes the preliminary absorption of the nitrous gases in feebly basic oxides, such as the oxides of zinc, copper, magnesium, and lead, and their subsequent release by heating to 500° C., while another [5] suggests the absorption of nitrous gases in wood charcoal. The gases are then recovered by treating the charcoal with steam, hot air, or an inert gas, or by heating *in vacuo*. For example, 1,000 parts of charcoal will absorb 122 parts by weight of nitric acid (as oxides of nitrogen) from a gaseous mixture containing 3 per cent. oxides of nitrogen by volume, and 133–174 parts from a mixture containing 5 per cent. by volume. By the subsequent heating, etc., 98 per cent. of the oxides can be regenerated.

The absorption of dilute nitrous gases by solid sodium carbonate has also been suggested.[6] The nitrite and nitrate so produced are treated with oxides or hydroxides of a metal of the alkaline earths. Nitrous gases are thus obtained in a concentrated condition. A method is proposed for the concentration of nitrous gases [7] by absorbing the dilute gases in sulphuric acid of such a strength that the nitrosyl sulphuric acid so formed is decomposed without the addition of any denitrating substance.

There are several important drawbacks to such methods of

[1] Eng. Pat. 28,614, 1903.
[2] Fr. Pat. 431,125, 1910.
[3] Fr. Pat. 404,630, 1908.
[4] Fr. Pat. 388,305, 1908.
[5] Fr. Pat. 423,760, 1910.
[6] Fr. Pat. 477,726, 1915.
[7] U.S.P. 1,291,909 and 1,316,950, 1915.

concentrating nitrous gases. If alkaline liquids are used as absorbents, large quantities of liquid have to be evaporated. If, on the other hand, dry metallic oxides such as zinc oxide or aluminium oxides are used, these are so weakly basic, that their absorbing effect is very small. In this connection Halvorsen [1] proposes to use as the absorbent a mixture of caustic soda and oxides of zinc, or iron, or aluminium, in the form of briquettes. The reactions taking place are then as follows :—

$$2NaOH + NO_2 + NO + [ZnO] = 2NaNO_2 + [ZnO] + H_2O$$
$$2NaOH + N_2O_4 + [ZnO] = NaNO_2 + NaNO_3 + [ZnO] + H_2O$$

If the temperature of the gases is not too high, the zinc oxide remains unaltered in the first stage, and by heating the resultant mixture to a higher temperature the following reactions take place, nitrous gases and sodium zincate being obtained.

$$2NaNO_2 + ZnO = Zn(ONa)_2 + NO + NO_2$$
$$2NaNO_3 + ZnO = Zn(ONa)_2 + [N_2O_5]$$

This residue of sodium zincate can be used repeatedly, as it acts as a mixture of ZnO and Na_2O, e.g.

$$Zn(ONa)_2 + N_2O_4 = NaNO_2 + NaNO_3 + ZnO.$$

This suggestion is theoretically attractive for use with very dilute nitrous gases. So far as can be ascertained, however, it has not yet been applied to large-scale practice, and it is probable, as is so often the case, that the practical difficulties in the way of the process outlined have outweighed any theoretical advantages. One of the chief troubles in all these processes in which solid oxides and salts are used as absorbents is caused by the presence of moisture in the nitrous gases being absorbed. Equilibria are set up, and the reaction is hence incomplete and the process inefficient. It is very difficult to see that such modifications of the absorption process are economical, since it would seem that any saving in the initial cost of tower construction would be more than compensated by the operation costs of such concentration processes. Furthermore, it appears to be cheaper to treat the products of absorption of dilute nitrous gases to obtain the final concentrated product required, rather than carry out any concentration

[1] U.S. Pat. 1,316,950, 1919.

process on the nitrous gases themselves. The position would depend to some extent, however, on the available market for the final product of absorption.

Liquefaction of Nitrous Gases. The concentration of nitrous gases by liquefaction has been frequently suggested for consideration in recent years as an adjunct to water absorption systems for nitrous gases, and particularly in plants where moderate concentrations of nitrogen tetroxide are available, i.e. in which liquefaction can be quickly and completely obtained by cooling alone without resort to increased pressures. There seems to be no information available in chemical literature as to the exact pressures and temperatures required to liquefy the nitrogen tetroxide from mixtures with varying amounts of air or inert gas. The curves shown in Fig. 36 are obtained from data calculated at the M.I.D. research laboratory, London, on the basis of vapour pressure measurements. They show the theoretical values of the temperature and pressure necessary to liquefy a given fraction of the N_2O_4 contained in a mixture with air, of known composition.

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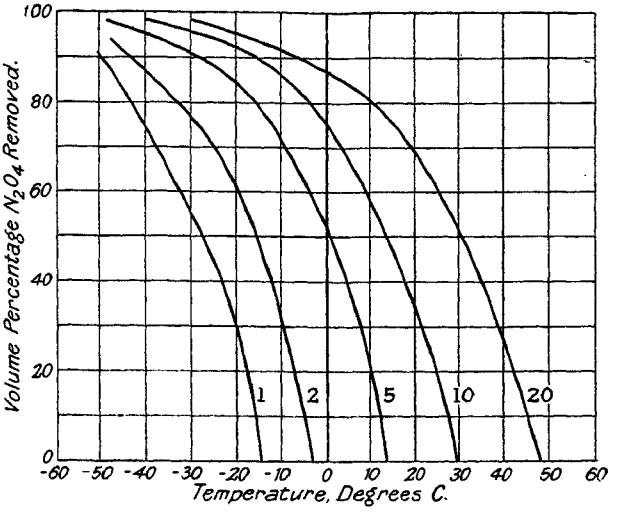
The further cooling of the trioxide or tetroxide results in the production of the solid oxides. Nitrogen tetroxide solidifies at $-10°$ C., and nitrogen trioxide at $-103°$ C. The two liquid oxides are completely miscible at 0° C., and, on cooling down to the point of solidification, deposit a eutectic mixture at $-112°$ C. This eutectic mixture corresponds to a composition [1] $NO_2 = 63{\cdot}6$ per cent. ; $NO = 36{\cdot}4$ per cent. (by vol.).

The importance of the separation of nitrogen tetroxide in the liquid state lies not only in the fact that it is in a very concentrated form, but also that its reaction with water appears to consist of an equilibrium represented by the equation

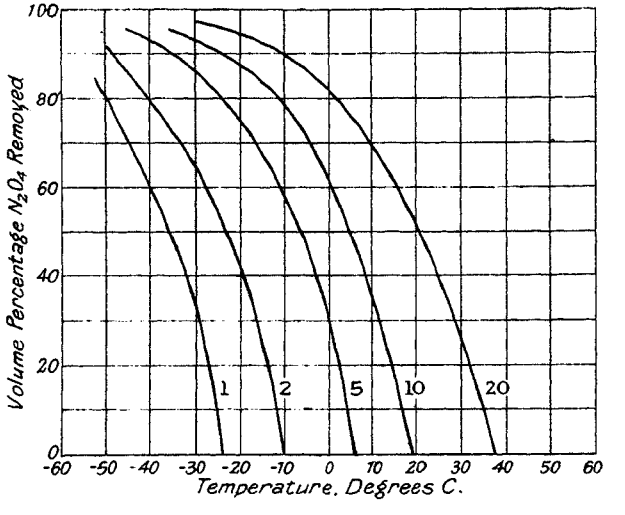
$$2N_2O_4 + H_2O \rightleftharpoons 2HNO_3 + N_2O_3.$$

By adding an excess of liquid nitrogen tetroxide to water, the concentration of nitric acid present may be made to reach any desired figure, even at ordinary temperatures (less than 20° C.). Furthermore, by bubbling oxygen into the mixture, the nitrogen trioxide present is slowly oxidized to the tetroxide so that the ultimate product may consist of nitric acid containing dissolved nitrogen tetroxide.

[1] Wittorf, *J. Russ. phys. Chem. Soc.*, 1904, **36**, 857.



A



B

FIG. 36.—Removal of N_2O_4 from a gaseous Mixture (*A*, 10 per cent., and *B*, 15 per cent.) by Cooling and Pressure [calculated from Vapour Pressure Data). The numbers on the curves refer to the pressure in atmospheres.

From *Physical and Chemical Data of Nitrogen Compounds*, M.I.D. Research Laboratory, University College, London.

This fact has led to the introduction of a number of patents covering the process. One such [1] states that liquid nitrogen tetroxide and oxygen at atmospheric pressure and temperature yield concentrated nitric acids with water. By employing a large excess of N_2O_4 (5–7 times the theoretical quantity required by the water present) nitric acids containing 90–95 per cent. HNO_3 can be obtained. Maxted [2] recommends the fractional liquefaction of the oxides of nitrogen from the oxidation

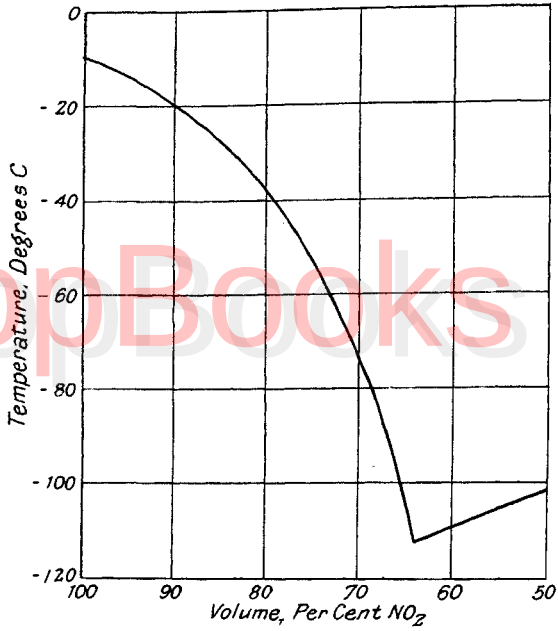


FIG. 37.—Freezing-point Curves of N_2O_4/N_2O_3 Mixtures (Wittorf).
From Abegg's *Handbuch der anorganische Chemie.*

of ammonia. The bulk of the water is removed between 50° and 100° C., and the further separation of the oxides of nitrogen carried out at appropriate temperatures below 0° C.

Another suggestion [3] is the addition of liquid nitrogen tetroxide to water, or dilute nitric acid, and subsequent addition of oxygen. To keep the water saturated, the pro-

[1] Eng. Pat. 126,704, 1919. [2] Eng. Pat. 127,343, 1917.
[3] Eng. Pat. 131,336, 1916.

portion of $N_2O_4 : H_2O$ should be at least 15 : 1. Two immiscible layers are formed. The upper layer, comprising $\frac{4}{5}$ of the total volume, consists of 98–100 per cent. HNO_3, while the lower layer consists of nitrogen tetroxide, containing 2–5 per cent. HNO_3. The process takes a long time at ordinary pressures, but may be accelerated by increasing the temperature to 30° C., and by compressing the oxygen up to 20 atmos. For example, an increase in pressure from 1 atmo. to 10 atmos. reduces the time required from 31 hours to 4 hours. A similar method of obtaining concentrated nitric acid is given in Eng. Pat. 4,345, 1915, in which liquid nitrogen tetroxide is added to dilute nitric acid and allowed to stand. The upper layer, containing nitric acid and nitrogen tetroxide, is purified by distillation, while the lower layer is treated with oxygen. For example, fifteen parts by weight of 81 per cent. HNO_3 were mixed with thirty parts of liquid nitrogen tetroxide. After settling, the upper layer contained 98–99 per cent. HNO_3, and the lower layer 75 per cent. HNO_3. The liquids should be well agitated, and the process carried out under reflux, or in an autoclave, to avoid loss of nitrogen tetroxide.

A similar patent to that of Maxted [1] is one [2] in which oxides of nitrogen are separated by fractional liquefaction, preferably in three stages. The first stage consists in cooling to − 10° C., when all the nitric acid present is condensed. The second stage is taken to − 30°–40° C., and the third to − 65° C., when all the N_2O_4 is solid. It is also proposed to use an inert solvent in the refrigerator during the liquefaction of nitrous gases.[3] The freezing-point of the solvent should be less than − 50° C., and its boiling-point greater than + 50° C. Such solvents as chloroform, carbon tetrachloride, and pentachlorethane are suitable. By dissolving the nitrogen tetroxide before it can form a non-conducting crust, they help to maintain the efficiency of refrigeration.[4] Another patent [5] states that by compressing the gases to a certain pressure and allowing them to expand to $\frac{1}{6}$ atmos., 90 per cent. of the nitrogen oxides are obtained in the liquid and solid forms. It is preferable to free the gases from carbon dioxide and water before com-

[1] *l.c.*
[2] Fr. Pat. 411,693, 1910.
[3] Fr. Pat. 421,022, 1909.
[4] See Guye, Fr. Pat. 404,630, 1908.
[5] Fr. Pat. 421,313, 1909.

pressing. No published information is available as to the cost and efficiency of recovery processes involving liquefaction, but they seem to offer an attractive alternative to the method of recovering nitrous gases as dilute nitric acid, and concentrating this by distillation with sulphuric acid.

There are three important disadvantages to such liquefaction processes.

1. Unless very low temperatures and relatively high pressures are used it will not be possible to liquefy the whole of the nitrogen oxides from a dilute mixture with air, and operation, even at the temperature of liquid air, would appear to be uneconomical.

In this connection some figures communicated to the author on the gases from ammonia oxidation, containing about 7 per cent. of nitrogen tetroxide (as NO_2) mixed with air, showed that 60 per cent. of the tetroxide could be liquefied at $-50°$ C. at atmospheric pressure, and 90 per cent. at $-80°$ C. This indicates that quite low temperatures would be required to secure efficient results from more dilute nitrous gases, as in the arc process, for example.

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2. The second disadvantage of the liquefaction process lies in the fact that both nitrogen oxides and nitric acid are present in the equilibrium mixture. The complete transformation of a given quantity of liquid nitrogen tetroxide into nitric acid will hence require several operations, in each of which there will be a certain loss of nitrogen oxides, both dissolved in the nitric acid and also as vapour.

3. The third disadvantage is that the use of oxygen for oxidizing the nitrous acid formed is expensive, and if air is used, a correspondingly greater loss occurs of nitrogen oxides mechanically carried away by the inert gas.

Against these disadvantages, combined with the cost of compression and the production of low temperatures, must be offset the commercial value of concentrated nitric acid containing 95 per cent. HNO_3, to dye-works and explosives works, and similar industries, where the mixed acids used require only a minimum percentage of water. For the general production of fertilizers, nitrites, etc., the method is obviously uneconomical.

Total Pressure of Gases. The velocity of oxidation

(V) of nitric oxide, according to the law of mass action, is proportional to the square of the concentration (or partial pressure) of the nitric oxide, and to the concentration (or partial pressure) of the oxygen,

$$\text{or } V = Kp^2_{NO}p_O.$$

Since the oxidation of nitric oxide is the greatest "time reaction" in the absorption system, it follows that an increase in the pressure of the gases in contact with the absorbent will greatly increase the velocity of this oxidation, and consequently the capacity of the system, the rate of absorption increasing approximately as the square of the pressure. In view of the fact that the great drawback to the present system of absorption of nitrous gases lies in the enormous cubic capacity which is required, entailing very high capital costs and large ground space, the possibility of working at increased pressures, and so reducing the size of absorption tower required to a fraction of the present capacity, is one which merits considerable attention from the nitrogen-fixation industries. Thus the absorption of nitrogen tetroxide at a pressure of two atmospheres would need approximately one quarter of the cubic capacity required for a given output that would be necessary if the gases were absorbed at atmospheric pressure. When it is considered that the capital cost of the absorption system represents more than 40 per cent. of the total cost of construction of an arc fixation plant, the importance of the modification is strikingly clear.

It must be emphasized that operation at increased pressures makes very little difference to the concentration of nitric acid of minimum vapour density, i.e. to the maximum concentration of nitric acid obtainable in the ordinary water absorption system. Roscoe[1] showed that the composition of the constant boiling nitric acid obtained from the absorption of nitrogen tetroxide in water varied from 68·0 per cent. HNO_3 at 735 mm. to 68·6 per cent. HNO_3 at 1,220 mm.

The difficulties which have prevented the use of increased pressures in absorption practice until recent years have been mainly due to the lack of suitable construction materials, which would resist weak nitric acid. This deficiency pre-

[1] *Annalen*, 1860, **116**, 203.

vented the construction of compressors and also of towers to withstand pressures greater than atmospheric. Stoneware has been almost the only available material for a long period of time, and though admirable so far as its resistance to nitric acid is concerned, is quite unsuitable for the construction of pressure-resisting apparatus of the type required. The development of iron-silicon alloys, however, has turned the attention of the industry again to the question of absorption under pressure, since the construction of suitable apparatus in such acid-resisting alloys presents no insuperable difficulty. It is very probable therefore that in the erection of new fixation plants, where aqueous nitric acid is the ultimate product required, the absorption system will be of much smaller cubic capacity, the towers built of iron-silicon alloy, and the system operated under a pressure of several atmospheres.

The operation of absorption towers under pressure has already been patented by the Norwegian Hydro-electric Company, but up to the present has not been developed by them, to the author's knowledge. It is interesting to observe, however, that Goodwin [1] states that in the new Häusser process of nitrogen fixation the volume of the tower absorption system had been reduced to one-sixtieth of the normal by absorption under $2\frac{1}{2}$–4 atmospheres pressure in chromium-nickel-steel or silicon-iron towers. The reduction to one-sixtieth with pressures only up to four atmospheres seems abnormal, but the important conclusion to be drawn is that the use of silicon-iron towers enables absorption at higher pressures to be carried on with very great economy in absorption plant costs.

A recent patent [2] states that highly concentrated nitric acid is obtained by treating water at 70° C. with a mixture of nitrogen tetroxide and oxygen under 20 atmospheres pressure. It should also be pointed out in this connection that the use of pressures sufficient to liquefy nitrogen tetroxide at ordinary temperatures (critical temperature 171·2° C.) will result in the establishment of the equilibria

$$2N_2O_4 + H_2O \rightleftharpoons 2HNO_3 + N_2O_3.$$
$$2N_2O_3 + O_2 \rightleftharpoons 2N_2O_4.$$

[1] *J. Soc. Chem. Ind.*, 1922, **41**, 394B.
[2] U.S. Pat. 1,273,991, 1918; cf. also D.R. Pat. 225,706, 1908.

In this case much higher concentrations of nitric acid are obtainable than under the conditions in which the ordinary absorption reactions apply, and a minimum vapour pressure nitric acid is obtained. It is also probable that with increased operation pressures the oxidation of nitrous acid and nitrogen trioxide by the oxygen dissolved in the solution would become an important reaction. Under normal conditions the oxidation of nitrous acid in solution by dissolved oxygen is negligible.

It has been proposed to absorb nitrogen tetroxide in charcoal.[1] A molecular proportion of water is then added, and finally oxygen at 3–5 atmospheres pressure.

Very little experimental information is available as to the quantitative relationship between increase of pressure and increase of capacity of the absorption system, and while operation at increased pressures seems to offer a number of theoretical advantages, it is very desirable to ascertain the relationship between the increase in operating costs entailed by the use of high pressures and the interest and depreciation charges on the extra capital cost of the ordinary absorption system.

Velocity of Gases. The velocity of the gaseous mixture through the absorption system requires careful adjustment. On the one hand, it determines the output of the system, and from an economic standpoint, therefore, should be as high as possible. On the other hand, increase in the velocity of the gases has an adverse effect on three important factors :—

(*a*) The amount of evaporation of nitric acid vapour by inert gas.

(*b*) The time of passage of the gas through the towers.

(*c*) The production of acid mist.

Of these the effect (*b*) is undoubtedly the most important, since it includes the two fundamental factors :—

1. The time allowed in the towers for the oxidation of the regenerated nitric oxide.

2. The time of contact between the gas and the liquid absorbent.

From what has already been stated, it will be seen that the velocity should not be greater than that which would allow for at least 50 per cent. of the regenerated nitric oxide to be

[1] Eng. Pat. 403, 1911.

reoxidized, or the capacity of the system will be affected unfavourably. For a similar reason, it is undesirable to increase the velocity of the gases to a stage which would be insufficient for the complete dissolution of the nitrogen tetroxide present in the liquid absorbent. Foerster and Koch [1] found that by passing nitrous gases mixed with air through nitric acid containing more than 50 per cent. HNO_3, a considerable effect was produced by variation in the velocity of the gases.

For example, the same gas mixture passed through 50 per cent. HNO_3 at 4·25 litres per hour gave a nitric acid containing 58·78 per cent. HNO_3; at 8·5 litres per hour 55·36 per cent. HNO_3; and at 17·0 litres per hour 53·95 per cent. HNO_3.

With more dilute acids than 50 per cent. HNO_3, the effect of the increase in velocity would, of course, be less, since the mass of water present would be greater, but the figures indicate the importance of the gas velocity on the efficiency of an absorption system. In modern tower systems where a very "free" packing material is used, i.e. where the percentage of unfilled space is high, it is particularly necessary to control the speed of the gases in order to secure sufficient contact between gas and wetted surface.

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It is almost self-evident that an increase in the gas velocity will result in increased evaporation of nitric acid, with consequent loss of efficiency. A particular type of evaporation effect also is the production of "acid mist" in the gas leaving the absorption system. This occurs to a limited extent in every absorption system, but increases very rapidly with the velocity of the gases. This acid mist, which is somewhat analogous to the sulphur trioxide mist produced in the concentration of sulphuric acid, will pass even through dilute alkaline solutions, and it is very difficult to recover the nitric acid carried away in this manner, except by electrical precipitation. It will be obvious, from what has already been said, that there is an optimum value for the velocity of nitrous gases of given composition, through an absorption system. This optimum velocity represents the maximum attainable output, for a minimum time of contact between gas and wetted surface and a minimum time of oxidation of nitric oxide.

It is not possible, with present data, to calculate the opti-

[1] *l.c.*

mum time of passage from purely theoretical considerations. It is different for every concentration of nitric oxide in air. Furthermore, it is evidently less than the minimum time required for the oxidation of the whole of the regenerated nitric oxide in the system. In some of the British Government factories (1915–19) fairly good results were stated to have been obtained by allowing a time of passage through the absorption system of approximately two minutes, this figure being obtained from the fraction [1]

$$\frac{\text{Cubic space not occupied by packing material}}{\text{Velocity of gas mixture in cubic feet per minute.}}$$

Expressed in another way, the figure of two minutes represents the fact that 75–100 cubic feet of "free" space are necessary for the absorption of 1 lb. of nitrogen tetroxide (as NO_2) per minute. This figure was derived from actual working results from small absorption towers filled with stoneware rings, taking the gases from a denitration plant. These gases contained 10–15 per cent. of nitrogen tetroxide (as NO_2).

Such a reaction time, which in the author's experience represents fairly good working under such conditions, is true only for the concentrations of nitrogen tetroxide mentioned. For a gas containing 1 per cent. of nitric oxide, for example, the free space required would be nearer 2,000 cubic feet. The time of passage would also be materially affected by such factors as temperature, type of packing, concentration of absorbing liquid, etc., etc.

The author has found that to obtain the same efficiency with gases from an ammonia oxidation plant containing 7–8 per cent. NO_2 (by vol.) a reaction time of approximately 20 minutes is necessary, and a recent communication on American practice also supports this figure. For the arc-process gas, containing 1 per cent. of NO, the time of passage required would be even longer, amounting to nearly 40 minutes if water absorption alone is used.

It is too commonly the case in practice to consider only the total volume of gases to be drawn through the absorption system, and the fan power required to pull them, without any reference to the intermediate distribution of velocity. This

[1] *Tech. Records Expl. Supply*, No. I, 1919.

may best be illustrated by considering the difference in pulling a given volume of gas through fine quartz containing a number of very fine channels, as compared with stoneware rings containing relatively large channels. The linear velocity of the gas in the two cases will be very different, although the volume movement may be the same. There will also be a very considerable difference in the efficiency in the two cases. Where possible, a very free packing should be used, and the draughting system provided with efficient dampers in order that the velocity of the gases may be controlled within fairly narrow limits.

For the fixing of gas velocity in practice, as many variables as possible, such as temperature, nature, and quantity of absorbent, etc., should be adjusted to the most favourable conditions, and the gas velocity increased until the percentage efficiency begins to drop. It will be found, as a general rule, that the suction head on the gases can only be very small, and for a "free" packing a suction of less than $\frac{1}{4}$ inch water gauge will usually be found to give efficient results, provided that the other factors are suitably adjusted. Under these conditions a linear velocity of 1–1·5 feet per second is usually obtained through an absorption tower of 3 feet diameter.

DropBooks

(2) Liquid Phase

In so far as the temperature of the absorbent is concerned, its influence on the liquid phase is very similar to that on the gaseous phase, since the latter readily takes up the temperature of the liquid on passing through the system. As previously stated, the only absorption reaction promoted by increase in temperature is the decomposition of nitrous acid, and there is no object in accelerating this reaction by raising the temperature at the expense of fundamental reactions which are much slower. There are several other variables affecting the liquid absorbent, however, which need to be considered. These are as follows :—

(*a*) The concentration of nitric acid in the absorbent.
(*b*) Its rate of circulation.
(*c*) The distribution of the absorbent.
(*d*) Turbulence.

Concentration of Nitric Acid in the Absorbent.

Foerster and Koch[1] showed that nitrogen tetroxide is not absorbed at a constant rate by water, but that the velocity of absorption is at first very rapid, acids containing 30–40 per cent. HNO_3 being quickly obtained. Above this concentration the rate of absorption falls off very quickly, the drop becoming most marked when the concentration of nitric acid in the absorbing solution is greater than 50 per cent. HNO_3. The curve shown in Fig. 38, plotted from their results, gives the

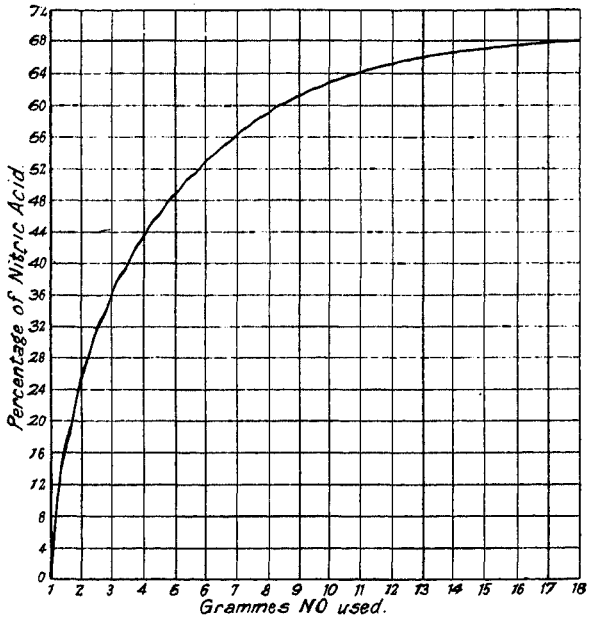

FIG. 38.—Curve showing Rate of Increase in Concentration of Nitric Acid produced by passing Nitrous Gases through Water.
Foerster and Koch, *Zeitsch. angew. Chem.*, 1908, **21**, 2161.

rate of absorption of the tetroxide as measured by the rate of increase in concentration of nitric acid in the absorbing solution. The flattening of the curve, as the concentration of the absorbing solution reaches 55–60 per cent. HNO_3, is very marked, and the very slow increase in concentration above this point is a fact of fundamental importance in the economic operation of an absorption system.

[1] *Zeitsch. angew. Chem.*, 1908, **21**, 2161.

It is found that the maximum percentage concentration of nitric acid obtainable by leading nitrogen tetroxide at temperatures above 0° C. into water is 68·4 per cent. HNO_3, at one atmosphere pressure. This is the composition of the mixture of nitric acid and water which has the least vapour pressure, and which forms a constant boiling mixture. When nitrogen tetroxide is led into nitric acid of this concentration, it merely dissolves, giving yellow solutions, and the N_2O_4 may readily be removed by blowing air through the solution.

It is not at first sight apparent why the maximum concentration of nitric acid obtainable should coincide with the mixture of minimum vapour pressure. The rate of formation of nitric acid from nitrogen tetroxide and water will depend mainly on the amount of " free " water in the absorbent at any given time, and consequently upon the stability of the several hydrates of nitric acid. The hydrate HNO_3, $2H_2O$ corresponds to an acid containing 64 per cent. HNO_3. At this concentration of acid it is probable, therefore, that the amount of " free " water in the solution, at ordinary temperatures, is very small. The rate of formation of nitric acid by the solution of nitrogen tetroxide will hence be very slow. On the other hand, Pascal [1] showed that although at 68·4 per cent. HNO_3 the percentage of nitric acid in liquid and vapour was the same, the vapour in contact with an acid containing 68 per cent. HNO_3 contains only 62 per cent. HNO_3. Nitrogen tetroxide would hence react with nitric acid vapour in the final stage of the absorption, causing the production of an acid of concentration identical with that of the constant boiling mixture.

The attainment of the final equilibrium is also affected by the velocity of the reaction

$$2NO + H_2O + HNO_3 \rightleftharpoons 3HNO_2.$$

This reaction, however, is dependent on the initial reaction between nitrogen tetroxide and water, and ceases when no further reaction between these latter substances takes place. Nitrogen tetroxide then dissolves unchanged in the nitric acid, but is easily removed by the passage of air or inert gas through the nitric acid, as was mentioned previously. For this reason, the nitric acid from absorption systems, even if it

[1] *Ann. Chim.*, 1921, 5, 253.

contains up to 68 per cent. HNO_3, contains only very little nitrogen tetroxide, being usually about 0·2 per cent. in plants where air lifts on the "emulseur" principle are used for circulating the acid absorbent. In such cases the agitation produced by the air in the acid causes the removal of nearly all the dissolved nitrogen tetroxide present. No figures are available as to the solubility of gaseous nitrogen tetroxide in nitric acid of different concentrations, but in general, the solubility increases with increase in the concentration of the nitric acid.

It should be emphasized that the constant boiling mixture previously mentioned is not a compound, its composition varying with the pressure. At 735 mm. it contains 68 per cent. HNO_3, and at 1,220 mm. 68.6 per cent. HNO_3, while by passing indifferent gas through the solution at ordinary temperatures, considerably lower concentrations of nitric acid are produced.

The results of Foerster and Koch are important as showing the relative value of dilute and concentrated nitric acid as absorbents for nitrogen tetroxide. It is a common practice in many works, where very dilute nitric acids (15–20 per cent. HNO_3) have to be disposed of, to use these as a feed to the absorption towers. By so doing the capacity of the absorption system is reduced to a proportionate extent if the same rate of feed is maintained. In the case of the small absorption towers, the water-inlet tower of the series usually attains a concentration of 15 per cent. HNO_3 at the bottom outlet. The use of a feed of nitric acid of this concentration, therefore, instead of an equal feed of water, is almost equivalent to the removal of one of the towers from the system. Nor can this effect be compensated altogether by increasing the rate of feed in proportion to the increase in concentration, since the wetted surface is more or less a fixed quantity, and is not proportionately increased by flooding the tower beyond a certain optimum point. Similarly, although the rate of renewal of the wetted surface is increased by flooding the tower, the increase is of little use when it exceeds the rate of dissolution of nitrogen tetroxide in the liquid absorbent.

It is clear, therefore, that the highest rate of absorption is obtained when the absorbing liquid contains only a small

percentage of nitric acid, and that from a purely chemical point of view it would be advantageous to use a separate water feed for each tower in the absorption plant. This would be uneconomical, however, as it would result in the production of large quantities of very dilute nitric acid. This leads to the second important point for consideration, viz. the highest concentration of nitric acid which should be aimed at in an absorption system.

The Optimum Output Concentration of Nitric Acid. From the curve in Fig. 38 it is evident that the rate at which nitrogen tetroxide is absorbed by nitric acid containing 60 per cent. HNO_3 to form 64 per cent. HNO_3, for example, is only approximately one-third of the rate at which the tetroxide is absorbed by 56 per cent. HNO_3 to form 60 per cent. HNO_3. It follows therefore that with the same absorption system, the output is reduced to one-third of its previous amount, by aiming at a final concentration of 64 per cent. HNO_3, as compared with 60 per cent. HNO_3. Expressed in another way, the extra absorption space required if the same total output is to be maintained at 64 per cent. HNO_3 instead of 60 per cent. HNO_3 will be very nearly twice the original. Valuable absorption capacity is often wasted in this way, for the sake of producing a nitric acid of a few per cent. greater concentration.

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It is not always possible to obtain acids of the order of 60 per cent. HNO_3. This will depend upon the concentration of the nitrous gases available. A gas mixture containing 1 per cent. by volume of nitric oxide could be made to yield an acid of only 45–46 per cent. HNO_3. A mixture containing 7 per cent. NO would yield 58–60 per cent. HNO_3 as a maximum.

In the case of gases from the arc furnace the maximum concentration available is practically within the limits of concentration of absorbent at which the rate of solution of nitrogen tetroxide is near the maximum. With higher concentrations than this, however, it is necessary to limit the concentration which shall be aimed at if efficient results are to be obtained.

It should also be borne in mind that the reduction of nitric acid by nitric oxide is more rapid, the more concentrated the nitric acid, and also the greater the mass of nitric acid present.

At equilibrium the ratio $\frac{HNO_3}{HNO_2}$ was shown by Veley[1] to be approx. 15·5.

Finally, the evaporative effect of the inert gases passing through the solution is much greater with concentrated nitric acids than with dilute acids, and offers a final reason for keeping the output concentration reasonably low, and so economizing absorption capacity. The concentration of nitric acid at which the rate of absorption of nitrogen tetroxide begins to fall off very appreciably is about 50–55 per cent. HNO_3, and it is found in practice that this is the optimum output concentration for most absorption plants.

Number of Towers to be operated in Series. The velocity of absorption of nitrogen tetroxide in moderately concentrated nitric acid has also an important bearing on the number of towers to be constituted as a "set" of absorbers. Suppose it is known, for example, that thirty-two absorption towers of given capacity are required for the absorption of a fixed amount of nitrous gases. The thirty-two towers may be connected up in series and the whole of the gas passed through them, or they may be divided into two sets of sixteen in parallel or four sets of eight and so on, and the gas divided up proportionately between them. There would be an evident disadvantage to the first arrangement, in the difficulty of draughting such a system owing to the resistance of the packing. If we assume that the filling material was very "free," and allowed a drop in pressure of $\frac{1}{4}$ inch of water through each tower, we should require at least 8 inches water suction at the fan, thus increasing very largely the possibility of leakage into the system and imperfect control of the gas near the gas-inlet tower. There is however a more serious disadvantage. Since the rate of attainment of a concentration of 40 per cent. HNO_3 is relatively rapid, the absorbing liquid will have attained this concentration, even if the maximum quantity of liquid is circulated, after the sixth or eighth tower of the series, in the case of the ordinary stoneware absorption tower. If we assume that we are dealing with nitrous gases of such concentration that they will yield an acid containing 58–60 per cent.

[1] *Chem. Soc. Trans.*, 1917, **111**, 415.

HNO_3 as a final product, it is clear that twenty-five of the absorption towers would be used for concentrating the acid from 40 per cent. HNO_3 to 55–58 per cent. (approx.). This would obviously be an uneconomical use of absorption capacity. It might be argued that sufficient water could be put down the towers to prevent a concentration of say 50 per cent. HNO_3 being reached until the twenty-seventh or twenty-eighth tower, and then the remaining four or five towers used for the concentration of the acid to 55 per cent. HNO_3. This is not possible in practice, however, since an excess of water over that required to give a completely wetted surface and a sufficient rate of renewal of wetted surface has little or no effect, i.e. the rate of absorption does not increase with increase in the circulating liquid beyond a certain optimum value, which is really a measure of the rate of dissolution of nitrogen tetroxide in water. For absorption systems composed of small stoneware towers, therefore, and with moderately concentrated gases, it is uneconomical to operate more than six to eight towers in series. Where the towers are very much larger, however, and the gases much more dilute, the conditions of operation may differ slightly, as a concentration of 40 per cent. HNO_3 is but slowly attained. Even in this case, however, it is preferable to operate the towers in small " sets " of two to four towers each, and to circulate liquid in each set until a definite concentration is obtained which may be passed on to the next set, and circulated again until it reaches a definite higher concentration. In addition the system will require independent draughting arrangements for each set of towers.

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Rate of Circulation of Acid. There are three general methods of operating an absorption system with respect to the feed of absorbing liquor:—

1. Passing once down the tower, or towers, the quantity of liquid necessary to give the required output of acid of given concentration.

2. Circulating an excess of liquid in each tower, and passing on only a part of this liquid to the next " stronger " tower in the series. The amount passed on corresponds again with the required output at a fixed concentration.

3. Flushing the tower intermittently with large volumes of liquid. This method is usually practised with very large

towers, and amounts practically to a continuous circulation, since the tower is never empty of liquid.

Considering the first of these methods, it is a matter of experience that if no circulation is carried out (and by " circulation " is meant the passage of the same absorbent down the tower more than once), the surface of the packing is incompletely wetted. In addition, the absorption is invariably uneven over the cross section of the tower, and thus causes inefficient working, while the rate of renewal of the wetted surface is insufficient.

The advantages of circulating the liquid absorbent are numerous, and the most important of them are as follows :—

1. There is greater certainty of the packing surface being homogeneously wetted.

2. A slight increase in the capacity of the system is obtained, owing to the effect of the increased mass of water.

3. The concentration of absorbing liquid in the tower is approximately constant, and therefore it is possible to maintain steady absorption conditions over much longer periods of time.

4. Such a system is better able to deal with an uneven load of nitrous gases than a non-circulating system. For example, in a nitric acid plant, the amount of nitrous gases coming to the absorbers may vary within very wide limits, depending upon the number of stills charging at a given time. If a non-circulating small feed is adjusted to the average quantity of nitrous gases passing, then at the " peak " periods a considerable loss of nitrous gases will occur unless such a " peak " period is watched for by repeated analyses, and this increases the operation cost. Furthermore, even if the water feed is increased, it takes a considerable time before the whole of the towers respond to the altered conditions, by which time the maximum-load condition has passed, and the feeds have again to be adjusted.

5. Greater agitation and scrubbing action are obtained.

6. The absorbing liquid in the end (water inlet) tower of the series is of lower concentration, and consequently the evaporative loss due to the escape of acid mist is much lessened.

All these points are of real importance in absorption practice. To offset these advantages, the circulation of absorbent

has two clear disadvantages. Firstly, the power cost is increased, and secondly the handling loss is somewhat greater. The circulation system is however the most efficient method of operating a counter-current absorption plant, since it is of fundamental importance to secure completely wetted packing, and the renewal of that wetted surface at a sufficiently rapid rate. Furthermore, the extra elasticity obtained, owing to the increased bulk of absorbent in the system, is very favourable to efficient operation.

The amount of liquid to be carried forward from tower to tower can readily be calculated from the amount of nitrous gases entering the system, and from the concentration of the final acid required. The amount to be circulated in each tower varies with the size of the tower, nature of packing, and incidentally with the means available for elevating the acid, etc. If the quantity of liquid kept in circulation in each tower is three to five times the amount of liquid passed on, the conditions in practice remain efficient and steady when the smaller types of absorption towers are used. In practice it is usual and convenient to keep the same bulk of liquid circulating in each tower, irrespective of the concentration of the absorbent, although theoretically the wetted surface requires renewing more frequently in the " weaker " towers of the system, owing to the rate of absorption being more rapid. When the conditions are adjusted, the concentration of the nitric acid in each tower of the set should remain practically constant.

With the larger types of absorption tower, the amount of liquid required to be circulated is very much increased.

The same system of circulation can be operated, however, in this case with advantage, although the number of large towers constituting a " set " is usually much smaller than is the case with the stoneware units. Several installations have sets of four towers, 80 feet × 20 feet, in a series. Acid is circulated in each, and a fixed amount passed forward. This is then used as circulating feed on another set of four similar towers, and so on.

In one of the American plants built during the recent war for the production of ammonium nitrate by the oxidation of ammonia, subsequent recovery of the oxides of nitrogen as dilute nitric acid took place in a tower system containing eight

absorption towers 60 feet high and 13 feet square, designed to turn out approximately 3,000 gallons of 58 per cent. HNO_3 per hour. The circulation on each tower was approximately twice this figure. The ratio of circulating liquid to output liquid is more commonly kept at a ratio of 1·5 : 1 or 2 : 1 in the case of the larger tower systems, chiefly because one of the difficulties of the smaller towers, i.e. effective distribution at the top of the tower, is more readily overcome in large towers since the liquid can be sprayed or pumped into the top of the tower under pressure.

In the case of the circulation of large quantities of absorbent, the question of the increased resistance to the passage of the gas must also be considered. Moscicki overcomes this by passing the gases horizontally through the packing material. He also derives from experimental data an empirical relationship

$$v = 1 \cdot 1qh$$

where v = volume of liquid in litres required to wet tower,
q = surface of packing in square decimetres,
h = height of tower in metres.

He also states that the flow of absorbent should be such that at least 0·7 litre of liquid per second should be fed in per square decimetre of packing. These figures were obtained for a gas from the arc process containing 1–1·5 per cent. NO, and cannot reasonably be applied to towers in which much larger concentrations of nitric oxide are being dealt with. The final figure for the linear velocity of the absorbent from Moscicki's experiments was 12·5 cm. per second, which is considerably exceeded, as is well known, in systems handling much larger concentrations of nitrous gases.

Distribution of Absorbent Liquid. The importance of securing efficient distribution of the liquid in the tower is almost self-evident, yet it is the factor usually neglected in small absorption systems, and the impossibility of being able to see inside the tower has led to a considerable amount of misconception as to what types of distributor are really efficient. The most common general methods of admitting liquid absorbent to the tower are :—

1. By a single pipe, gravity fed, dropping on to a distributing plate.

2. By feeding the liquid into an overflow plate, such as is used in the Glover tower, and so delivering a number of small streams of liquid into different parts of the tower.

3. Spraying, or blowing in the liquid under pressure, either through an atomizing jet, or a rotating distributor, or on to a splash plate.

The distributing plates used in practice vary in design with the diameter of the tower. For stoneware towers up to 3 feet diameter the types shown in Fig. 39 are commonly used, for

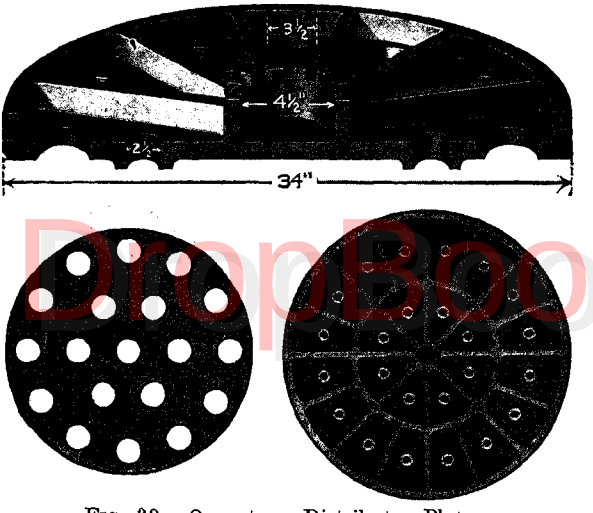

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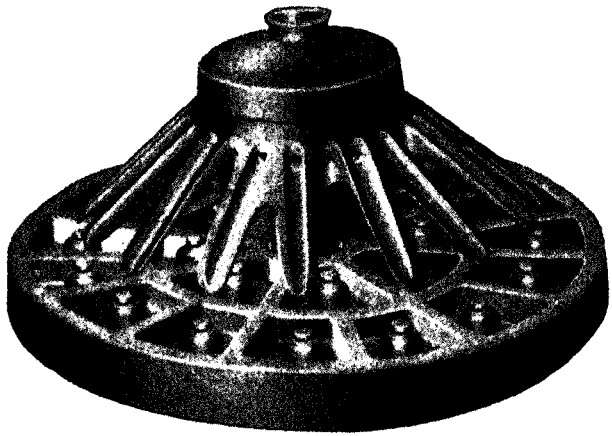
FIG. 39.—Open-type Distributor Plates.
Maurice A. Knight.

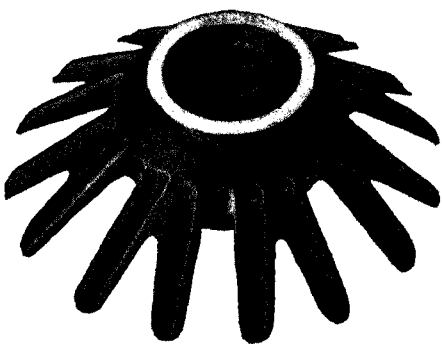
the larger towers some such device as shown in Fig. 40. The principle of all such distributing plates is to deliver a large number of small streams of liquid evenly over the cross section of the tower.

It is evident that the defects of such distributors will be mainly caused by inaccurate levelling, and the uneven working due to the deposition of sediment in the small channels. With a well-constructed distributor the difficulty of levelling is not perhaps very great, but it is difficult to avoid continuous trouble due to grit, etc. All gravity-fed towers are liable to suffer in this respect. In towers where only a single jet of liquid is run in, it is very unlikely that even distribution of the

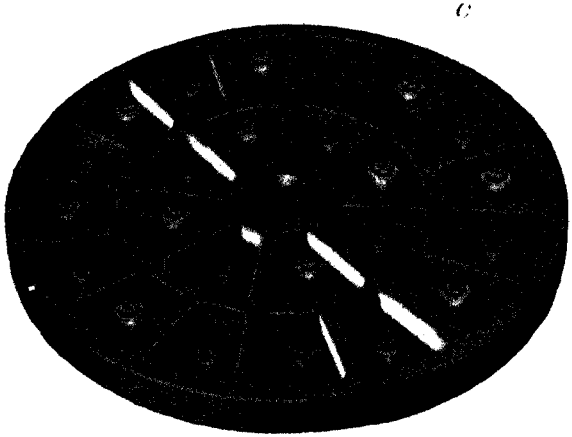


A

B



C



D

FIG. 40.—Closed-type Acid-proof Distributor.

A, assembled. *B*, *C*, *D*, separate parts.

Maurice A. Knight.

liquid will take place, unless the filling material is of small diameter, spherical in shape, homogeneously packed, and the tower of small diameter. With many small towers in practice, however, the result obtained is similar to that shown in Fig. 70, (p. 196), the tower being incompletely wetted for several feet down. This defect can be overcome to some extent by increasing the distance between the distributing plate and the top layer of packing, in order to cause the streams to splash, but this cannot be done efficiently in small towers, as the packed space is comparatively small. A depth of 1 foot to 1 foot 6 inches is usually left for this purpose.

The difficulty of securing good distribution in a square tower is greater than with a tower of circular section, owing to the "collecting" action of the corners in the square tower, which tend to send the liquid down in relatively large streams. The difficulty also increases with increasing diameter of the tower.

It has been suggested that a greater efficiency of initial distribution would be obtained if the absorbent were caused to pass through a layer of fine sand, from which it would be delivered on to the packing in a large number of droplets, homogeneously distributed, owing to the capillary action of the sand particles. It seems a fruitful field of investigation to examine the possibility of utilizing capillary action for initial distribution instead of depending on carefully adjusted constant-level apparatus.

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It is sometimes the practice also to fix intermediate distribution plates at different levels in the tower. The object of this is apparently to collect up the liquid after it has fallen through a certain distance in the tower, and redistribute it, and also to give intermediate support to the packing. The procedure is, however, erroneous, since it is desirable to maintain the liquid continually as a thin film over a large area, rather than to collect it up into streams of relatively little surface. When such a device is considered necessary in a tower, it is time to consider whether the filling material is efficient so far as distribution of gas and liquid is concerned. It may be taken as a general principle that wherever a liquid absorbent is delivered on to packing material in the form of a pencil of liquid, the danger of channelling is always accentuated.

There is little doubt that the best initial distribution of the

absorbent is obtained when the liquid is sprayed or pumped into the tower under pressure, and especially if an atomizing jet is used. Whether such devices are economical in practice, however, is open to doubt. Fine sprays, for example, are quickly put out of action by grit and slime. In the case of high towers (60–80 feet) a very heavy initial pressure is required to give 10–15 lb. sq. in. necessary at the top of the tower for efficient spraying, and it is difficult to obtain acid mains which will withstand the pressure for any length of time, or even to obtain pumps or blowing eggs for nitric acid which will work satisfactorily under such conditions.

The gravity feed, therefore, in spite of its relative inefficiency, is more reliable, and it is reliability which is a first essential in the flooding of absorption towers, since a failure in the supply means heavy losses of fixed nitrogen.

The use of sprays of liquid for absorption in unpacked towers is quite logical, although it is difficult to see that such apparatus would be economical, as compared with the packed-tower system. Dawson [1] projects sprays of water or weak acid from the bottom of an unpacked tower, parallel with the gas flow. A diagram of his apparatus is given on page 177.

The use of unpacked towers for the absorption of nitrous gases has been suggested by a number of workers. The disadvantages of such a system would be:

(*a*) The towers would have to be of considerable diameter, or the greater part of the absorbent would be caught on the walls, and run down as a stream of small surface.

(*b*) In towers of sufficient height to allow the necessary time for the oxidation of nitric oxide, the fine particles would aggregate into large drops of relatively small surface, after having fallen a certain distance.

(*c*) Practically no mixing of the gas would take place.

(*d*) The cost of producing the necessary surface of contact between gas and liquid would be very much greater than in the case of the packed tower, since the volume of gas passing up the tower is enormously greater than the volume of liquid absorbing it.

For these reasons the use of unpacked towers for the absorption of nitrous gases by water is quite uneconomical, though

[1] Eng. Pat. 120,869, 1919.

the efficiency of distribution of the liquid may be very high. The same arguments would not apply with such force, however, if an alkaline absorbent, such as milk of lime, were used. Here the danger of the packed tower becoming choked with solid is sufficiently acute to justify in part the elimination of packing from the tower.

Turbulence. It is being recognized that turbulence, which has the effect of producing an emulsion of liquid and gas, plays an important part in promoting absorption efficiency. The turbulence produced in an absorption tower depends upon :—

1. The type of packing used, i.e. the changes of direction occurring in a given section of packing, the presence of liquid traps, etc.
2. The velocity of the gases.
3. The nature of the absorbing solution.
4. The amount of absorbent being circulated.
5. The distribution of the absorbent.

Most of these points have already been considered under various headings. The surface tension of the absorbent has an important effect on turbulence, and substances which increase the surface tension are advantageous in this respect, although otherwise undesirable, and in fact uneconomical. They have found some application, however, where alkaline absorbing liquids are used. In Fr. Pat. 375,342, 1907, the addition of soap to such alkaline liquids is recommended, whereby an enormously increased surface is obtained. The gas, furthermore, is introduced in jets in order to promote turbulence.

The Use of Ozone in Absorption Practice. The action of ozone on nitrous gases has been the subject of investigation by a number of workers. Foerster and Koch [1] passed a mixture of nitrogen tetroxide and ozonized air into water, and found that it was quite possible to obtain nitric acids containing over 80 per cent. HNO_3, i.e. the nitrogen tetroxide was effectively oxidized to nitrogen pentoxide by ozone. Investigations on the action of ozone on nitrous gases have been also carried out by Russ and Ehrlich.[2] They found that nitrogen

[1] *Zeitsch. angew. Chem.*, 1908, **21**, 2209.
[2] *Zeitsch. Elektrochem.*, 1914, **20**, 45 ; see also D.R. Pat. 266,345, 1912.

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could be oxidized directly to nitrogen pentoxide in the silent electric discharge, in the presence of ozone, which latter may also be produced *in situ* by the discharge. If air is drawn comparatively quickly through the discharge tube, both ozone and nitrogen oxides are produced, the ratio of the two substances $\frac{N_2O_5}{O_3}$ 0·019, so that ozone is in considerable excess. By exposing the mixture to the action of the silent discharge until the ozone has been completely used up, however, a far-reaching oxidation of the nitrous gases to nitrogen pentoxide occurs.

In one experiment a Siemens tube, with a distance of 4 mm. between the electrodes and a discharge space of 140 c.c., was employed, the tube being externally water-cooled. The discharge was produced by a current at 15,000 volts, and 50 periodicity. A mixture of equal volumes of oxygen and nitrogen was led through the tube at a rate of 4 c.c. per minute under atmospheric pressure. The concentration of N_2O_5 obtained was approximately 200 milligrams per litre, and by leading the gases into water a pure nitric acid resulted.

Russ and Ehrlich found that when a silent discharge was passed through stagnant mixtures of nitrogen and oxygen, the amount of pentoxide produced depends on the initial volume percentage of oxygen in the mixture. Further details as to the formation of ozone in the arc process, and its action on nitrogen oxides, may be found in a paper by Russ.[1] The use of ozone in absorption practice has not, as yet, developed beyond the experimental stage, owing to the low concentrations obtainable and to the relatively high cost.

In many oxidation processes ozone appears to act catalytically, all three oxygen atoms being effective. The phenomenon is essentially similar to that of autoxidation. Some experimental work carried out by the author with N. Sheldon, on the oxidation by ozone of nitrous acid in waste acids from explosives manufacture, showed that oxidation of nitrous acid did not occur in the solution, but that the oxides of nitrogen in the vapours carried forward were oxidized to nitrogen pentoxide. It was found, however, that only one-third of the ozone molecule was effective in the oxidation of

[1] *Zeitsch. angew. Chem.*, 1912, **25**, 566.

nitrogen tetroxide to the pentoxide. It is clear, therefore, that the use of ozone commercially, for facilitating the absorption of nitrogen tetroxide, is uneconomical. The concentration of ozone available in large-scale operation is of the order of 2·5 gram per cubic metre. In dealing with a gas mixture containing 10 per cent. NO_2 by volume, or approximately 200 gm. per cubic metre, the amount of ozone required for the oxidation of this gas to N_2O_5 would be approximately 140 grams, and would be associated with 56 cubic metres of gas. The cost and difficulty of multiplying the volume of gas dealt with by this figure renders it unsuitable as a commercial proposition, although it is very attractive as a means of facilitating the absorption of nitrous gases.

The Influence of Chlorine on the Absorption of Nitrous Gases. The possibility of speeding up the absorption cycle is the motive behind a great deal of the recent research work carried out on absorption. It is obvious from what has been said before that it is the regeneration and oxidation of nitric oxide in the cycle which constitutes the main "time reaction," and although a number of patents suggest the removal of the regenerated NO, and its oxidation in special chambers, before admission to the tower system, the modification does not increase the capacity of the system.

The action of chlorine in the cycle has been specially mentioned, because it is almost invariably a constituent of the nitrous gases passing to the absorption towers, in the pot process for nitric acid manufacture, owing to the presence of sodium chloride in the nitre used.[1] For example, the following analyses were obtained from the nitrous gases passing to the absorption system from such a nitric acid plant.

TABLE 29

N_2O_4 as grains HNO_3 per cub. ft.	HNO_3 as grains HNO_3 per cub. ft.	Free Chlorine grains per cub. ft.	Combined Chlorine as NOCl, etc. grains per cub. ft.
108·2	12·9	4·78	3·58
91·7	13·3	4·61	3·43

[1] Webb, *J. Soc. Chem. Ind.*, 1921, **40**, 162T.

By examining the nitric and hydrochloric acid content of the acid running from each tower of the system, under steady conditions of equal flow down each tower, the results obtained in Table 30 were obtained, and have been expressed graphically in Fig. 41.

An examination of the curves in Fig. 41 will show that in each case the greatest increase in the rate of absorption of nitric acid is coincident with the greatest decrease in the concentration of hydrochloric acid, and it is clear therefore that chlorine has a marked accelerating effect on the absorption. This may be explained in the following way :—

Nitric acid forms two main hydrates, HNO_3,H_2O and $HNO_3,3H_2O$, corresponding to 77 per cent. HNO_3 and 54 per cent. HNO_3 respectively. At some concentration a little above 54 per cent. HNO_3, therefore, the " free " water in the system tends to become very small.

Furthermore, it can be shown that the reaction

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$$

takes place only with nitric acids of concentration greater than 55–60 per cent. HNO_3, i.e. containing little or no " free " water. In the towers in the absorption set, containing nitric acids of concentration greater than 55 per cent. HNO_3, therefore, all the hydrochloric acid present in the inlet gases is converted into a mixture of nitrosyl chloride and chlorine. When the gas, on passing through the system, meets with absorbing liquid containing less than 55 per cent. HNO_3, the following reactions take place :—

$$NOCl + H_2O = HNO_2 + HCl$$
$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$
$$HNO_2 + HClO = HNO_3 + HCl.$$

The nitrous acid formed by the initial absorption of nitrogen tetroxide in water does not regenerate nitric oxide therefore, but is oxidized by the hypochlorous acid produced by the chlorine present. This results in a very rapid acceleration of the rate of absorption, the nitric acid increasing to a concentration of over 50 per cent. HNO_3 in the particular tower at which the conditions occur. Above this concentration, the formation of nitrosyl chloride again sets in, three molecules of HCl being removed for one molecule of HNO_3. The gases

TABLE 30

Number of Tower.	Twaddell of Acid at Base. ° Tw.	Per cent. HCl.	Per cent. HNO_3.	Increase in percent. HCl starting from Water-inlet Tower.	Increase in percent. HNO_3 starting from Water-inlet Tower.
Water Feed = 14 gallons per hour.					
1 (gas inlet)	84·5	0·13	[71·1]*	— 0·8	[11·3]
2	73·5	0·21	59·8	— 1·7	12·6
3	56·0	1·9	47·2	— 7·4	16·6
4	39·5	9·3	30·6	— 3·0	5·5
5	32·0	12·3	25·1	— 1·5	2·7
6	29·5	13·8	22·4	0·0	1·5
7	27·0	13·8	20·9	— 0·1	5·0
8 (water inlet)	24·0	13·9	15·9	0·0	0
Water Feed = 8·5 gallons per hour.					
1	91	0·11	[75·2]*	— 0·04	[5·3]
2	87	0·15	[69·9]*	+ 0·01	4·8
3	84	0·14	65·1	— 0·09	5·2
4	78·5	0·23	59·9	— 0·9	10·8
5	66·5	1·1	49·1	— 8·4	24·6
6	42·5	9·5	24·5	— 6·7	14·6
7	30·5	16·2	9·9	— 0·3	4·5
8	24·5	16·5	5·4	0·0	0·0
Water Feed = 11 gallons per hour.					
1	87·5	0·01	[74·0]*	0·0	[7·5]
2	81·5	0·01	66·5	0·0	3·7
3	76·5	0·01	62·8	— 0·5	8·8
4	68·0	0·51	54·0	— 3·5	18·5
5	47·5	4·02	35·5	— 6·3	17·6
6	32·5	10·31	17·9	— 1·7	6·2
7	25·0	12·03	11·7	+ 0·51	5·4
8	17·5	11·52	6·3	0·0	0·0
Water Feed = 4 gallons per hour.					
1	90	0·09	[78·05]*	— 0·04	7·48
2	82	0·13	[70·97]*	— 0·15	12·26
3	71·5	0·28	58·31	— 4·7	19·94
4	51·5	4·97	38·37	— 1·9	7·0
5	31·5	6·80	31·30	— 4·8	9·2
6	29·5	11·60	22·10	— 3·1	6·0
7	27·5	14·70	16·10	— 0·3	4·7
8	24·5	15·00	11·4	0·0	0·0

* In these towers nitric acid vapour was carried with the gas from the plant into the tower.

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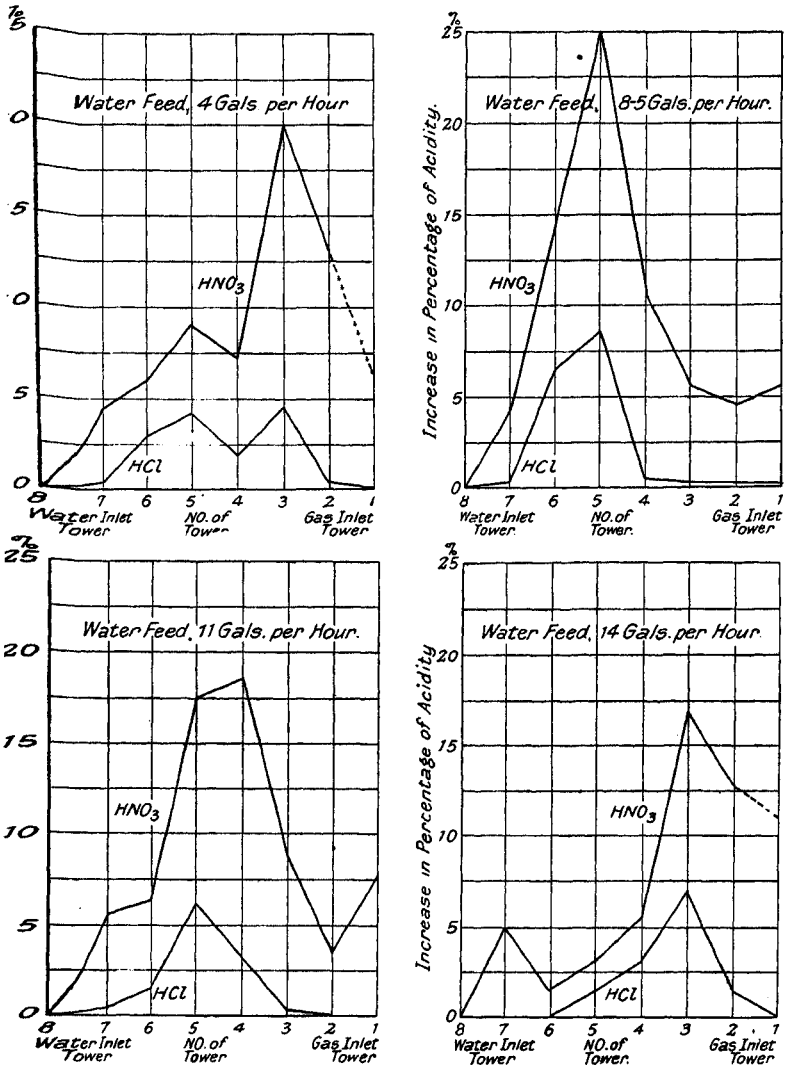
Water Feed, 4 Gals per Hour
HNO3
HCl
Water Inlet Tower
NO. of Tower
Gas Inlet Tower
Water Feed, 8·5 Gals. per Hour.
Increase in Percentage of Acidity.
Water Feed, 11 Gals. per Hour.
Water Feed, 14 Gals. per Hour.

FIG. 41.—Influence of Chlorine on the Absorption of Nitrous Gases by Water.

Webb, *J. Soc. Chem. Ind.*, 1921, **40**, 162T.

aving the tower consist of nitrogen oxides, nitrosyl chloride, nd hydrochloric acid, but no free chlorine.

The concentration of the nitric acid emerging from the tower

in which this increase occurred should be, as stated above, about 50 per cent. HNO_3. The actual concentrations of nitric acid obtained in the particular tower in which the sharp rise in concentration occurred were as follows :—

1. 59·0 per cent.	4. 53·4 per cent.	7. 49·1 per cent.
2. 56·3 ,, ,,	5. 59·0 ,, ,,	8. 54·0 ,, ,,
3. 50·7 ,, ,,	6. 58·3 ,, ,,	

Analysis of the exit gas to the system showed 9·5 grains per cubic foot as chlorine and 7·1 grains as nitric oxide, i.e a ratio of NO : Cl = 1 : 1·2. The ratio of NO : Cl in NOCl = 30 : 35·5 = 1 : 1·2 (approx.).

While chlorine is not a suitable substance for the acceleration of the reaction in large-scale practice, its action suggests that the present enormous size required for absorption towers may yet be considerably reduced by development of methods in which such a principle is applied, particularly where very dilute nitrous gases have to be dealt with.

Catalytic Oxidation of Nitric Oxide. During recent years considerable attention has been given to the possibility of catalysing the comparatively slow oxidation of nitric oxide to the tetroxide. In this connection the work of Classen [1] is important. It is claimed that the oxides and nitrates of nickel and cobalt have a catalytic effect on the rate of oxidation of nitric oxide by atmospheric oxygen. The catalyst is prepared in a pure condition and dried at 100°–120° C. The oxidation is allowed to take place at ordinary temperatures. No figures have been published as to the acceleration of velocity which is obtained. The presence of ozone in the atmospheric oxygen is very beneficial to the rate of oxidation. The process does not seem to have been adopted by the nitrogen industry as a whole up to the present, in spite of the apparent advantages of the process.

[1] U.S. Pat. 1,178,440, 1916.

CHAPTER III

CONSTRUCTION OF ABSORPTION TOWERS

The brief survey of some of the theoretical considerations underlying modern absorption practices will have served to emphasize the fact that although the chemical reactions involved are apparently simple, the adjustment of the process for efficient operation requires considerable care and attention to detail. In this chapter it is proposed to give a general account of some of the types of construction used in practice to absorb the nitrous gases resulting from various industrial operations. In many such cases the questions of prime cost and availability of materials have outweighed purely theoretical considerations of efficiency, and this must be borne in mind in estimating the value of a particular type of construction, or the efficiency of an accessory to the general absorption system. The points considered deal almost exclusively with water absorption systems, since other types are relatively uncommon, though many modifications of the ordinary counter-current process exist.

It must also be emphasized that the nitrogen-fixation industries in this country are only in their infancy. Almost all the absorption plants at present in operation are recovering nitrous gases existing as a by-product and not as the main chemical result of a series of industrial operations. In most continental countries, on the other hand, nitrogen-fixation plants have been developed to a considerable extent, as an integral part of agricultural development, and also as being essential to economic independence. The view-point of industry in the two cases, therefore, is not identical, and consequently the development of the absorption systems in the two cases has not been parallel. In fact, so far as this country is concerned, the development was almost negligible,

until the recent European war, when attention was summarily called to the importance of the problem. For this reason, important general differences exist in the types of construction in general use, and as far as possible an endeavour has been made to indicate these differences when describing plant operation. Furthermore, the constructional details of plants in other countries have not been universally available, and resort has been made in such cases to published information, where the accuracy could be reasonably checked.

Small-type Absorption Towers

It is possible to distinguish in practice two types of absorption tower for nitrous gases :—

(*a*) Small stoneware units, which are used for relatively small quantities of concentrated nitrous gases.

(*b*) Large brick, stone, or granite towers for dealing with large volumes of dilute nitrous gases.

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There is no fundamental difference between the two types of tower above, the division existing mainly owing to the limitations of stoneware as a construction material for tower work. It is a convenient division, however, as many of the details of construction are appreciably different in the two cases. The first type is the most commonly used in this country, the use of the larger towers being limited to the nitrogen-fixation and ammonia-oxidation industries. The constructional details of the smaller tower will first be briefly considered.

Site of Absorption Towers. The main factors which should govern the choice of a site for the absorption system are as follows :—

1. The facilities for transport and storage of the weak nitric acid produced.
2. Convenient water supply.
3. Absence of underground pipe lines.
4. Suitable draughting arrangements.
5. Facility for technical supervision.

The distance of the absorption plant from the source of supply of the nitrous gases is normally a factor which should be increased rather than diminished, since the additional length

of pipe run so obtained is advantageous, so far as mixing and oxidation of the nitric oxide are concerned. It is inadvisable to erect absorption towers near to underground iron pipes, since a certain amount of accidental leakage always occurs, such as overflow of the acid from elevator systems, the breaking of glass carboys, etc. Considerable trouble is often experienced from lack of attention to this simple precaution.

The water supply to the absorption system is very important and an adequate pressure should be available at the site chosen.

The draughting of an absorption system is usually carried out by suitable fans, but quite commonly small absorption sets have to rely on chimney draught, and it is advisable therefore to place the set at a convenient position from the chimney so that the draught may be regular, and the length of pipe run after the set as small as possible. In special cases other factors may have to be considered. In systems attached to denitration plants, for example, it is common practice to use the weak condensed acid from the denitration plant as a feed down the absorption towers. In consequence, the handling of weak nitric acid between the two systems should be cut down to a minimum.

The ground on which the absorbers are erected should be well drained, with conduits in acid-proof brick to drain the acid leakage to a central well, from whence it may be elevated and stored. The floor below the brick piers on which the towers stand should be laid with acid-proof brick and acid-proof cement.

Brick Piers. Each set of towers is supported by a brick pier, the height of which is governed by the height of the towers, the fall required for the air lifts for elevating the acid (if such are used), the level of the acid receiver, and the use of intermediate acid storages.

Of these factors the most important is the fall required for the Pohle lifts. This is usually made one-third the total height to which the acid has to be elevated, so that the piers are about one half the height of the tower. Since the small stoneware towers vary in height from approximately 12 feet to 20 feet, brick piers of 6 feet to 12 feet high are usually sufficient. It is inadvisable to go beyond 15 feet to 20 feet high for these piers, since economy of construction can be obtained by suitable

modification in the acid-elevating apparatus, for towers of this height.

The base of the pier should be laid on concrete, which is given a slope to suitable drains for collecting acid leaks, overflows, etc.

FIG. 42.—Stoneware Absorption Tower.
Oates & Green, Ltd.

The bricks should be laid preferably with a good acid-resisting cement, since, although the prime cost is higher than with ordinary cement composition, the latter disintegrates very rapidly, and may cause serious lifting in the brickwork if attacked by acid. For similar reasons, the bricks should be of good acid-resisting quality. A good Staffordshire blue brick is quite resistant to nitric acid and has quite a long life, but care must be taken that it is not a " salt glaze " brick which is only partially burnt through. Such bricks are liable to split and disintegrate, when once penetrated by the acid.

It is also advisable to coat the top of the pier with a layer of asphalt 2–3 inches in thickness. This asphalt should be tested for its resistance to nitric acid, as the quality of the ordinary commercial material varies very considerably.

The internal diameter of the towers is usually 2 feet 6 inches to 3 feet 6 inches, the commonest type being those of 3 feet diameter. The tower consists of four or five stoneware sections each of diameter 3 feet and depth 2 feet 6 inches. The bottom section rests in a saucer of depth varying from 9 inches to 21 inches, depending on the makers of the towers. This saucer forms an auxiliary storage of circulating liquor in the tower itself. It is provided with at least two stoneware bosses into which are fitted stoneware taps, one of which feeds the

acid-elevators, the other serving either as a drainage cock or for feeding an auxiliary elevator. The total height of the towers hence varies between 12 and 15 feet, or between 20–30 feet, taking into account the brick piers on which the towers stand.

The socket joint between each section of the tower is filled usually with a soft putty, although hard cements are sometimes used if the system is not subject to wide fluctuations of temperature. The usual method of packing these joints consists in caulking in first a coil of $\frac{1}{2}$ inch asbestos rope, and then covering this with a soft putty composed of linseed oil, china clay, and flock asbestos. Alternatively a thick paste of asbestos fibre and sodium silicate solution (1·35–1·40 sp. gr.) is rammed in. The top of the soft putty, or the cement layer, is then

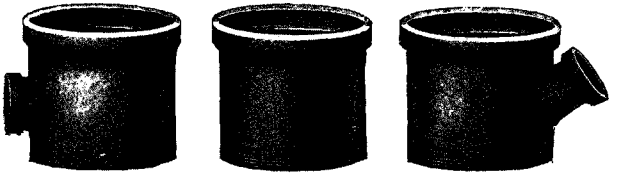

FIG. 43.—Sections for Stoneware Tower.
Oates & Green, Ltd.

covered with a mixture of tar and pitch containing about 5 per cent. by weight of plaster of paris. This mixture sets firmly, and serves to protect the cement or putty from the weather. It must be emphasized that a hard cement should only be used for filling joints in stoneware when there is no likelihood of temperature variations taking place, and where the prospect of the towers having to be dismantled is remote, since it is almost impossible to separate the sections without breakage when once such a cement has set.

If a well made, scientific packing is used in the towers, there is no need of supporting each tower section at the collar, but where quartz or similar heavy packing is used, it is advisable to carry the weight of each section on a wooden collar forming part of an external framework. A similar device is also adopted in the case of stoneware mains, which would otherwise be insufficiently rigid.

Packing Material. The weight and strength of a packing

of ordinary scientific design is such that the elements can be built up right from the base of the saucer, without requiring intermediate supports.

The heavier quartz packing is preferably taken on about 12 inches of chequer brickwork resting in the bottom saucer. In addition it is often the plan, with both types of packings, and quite essential in the case of quartz and coke packings, to carry the packing material in each tower section on a circular slate slab pierced with a number of holes. This method of supporting the packing is claimed to have several advantages, of which the most important are :—

1. It is unnecessary then that each section of the tower should be completely filled with packing, and consequently small unpacked spaces can be left in the tower, which facilitate the progress of some of the absorption reactions.

2. The mixing of the gas is rendered more efficient.

3. If channelling is taking place in the tower, the presence of the intermediate plates tends to minimize its effect.

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As was pointed out in the previous chapter, however, the disadvantage attached to the use of such supporting plates, with a good scientific filling, lies in the fact that the water which has been distributed by capillary action is forced to collect again in small streams, which fall through the tower for some distance before the liquid is again homogeneously distributed.

Distributing Plates. On the top of the packing is usually placed a distributing plate. Several types of these are shown in Figs. 39, 40, and 44.

The type of distributing plate to be used depends mainly upon the total quantity of liquid to be passed down the tower. Generally speaking, the greater the quantity of liquid, the easier it is to distribute efficiently.

The distributing plates shown in Fig. 44 are for small towers and small liquid flows, and the object aimed at is to secure a large number of small streams, evenly distributed. It is evident therefore that very careful levelling of the plates is necessary and also that apertures should be accurately proportioned. In the types of distributor shown an attempt has been made to secure efficiency with the simplest possible type of construction. There is no doubt however, that modifica-

tions are possible which would tend towards the ideal distributing plate, although these often demand more intricate (and hence costly) construction.

A French patent [1] suggests the use of a layer of filtering material such as sand in the top of the tower, in order to give a large number of points for the liquid to drop underneath. The filter also removes solid particles and tends to prevent channelling in consequence. In such a distributor, the capillary action of the material is the most potent factor in securing the distribution of the liquid, and the liquid is homogeneously

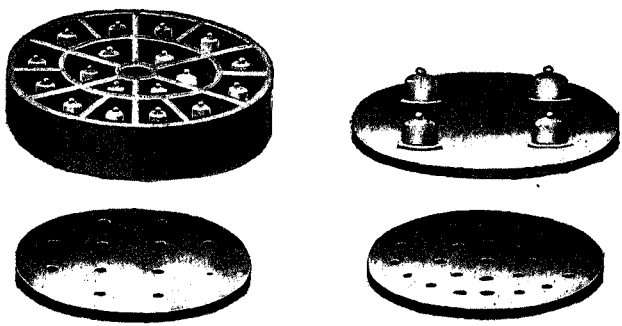

FIG. 44.—Types of Distributing Plates for Small Towers.
Oates & Green, Ltd.

distributed throughout the mass. Although the use of sand in the tower, for such a purpose, has many practical disadvantages, it must be admitted that the present gravity-feed system of acid distribution in small absorption towers leaves much to be desired from the point of view of homogeneity.

Above the top of the packing a space of about 18 inches depth is usually left to facilitate the mixing of the gases. It is an improvement to place the distributing plate *above* this unpacked space, the liquor distribution being much more efficient if this is done. This is actually effected in some towers by fitting a flat dome piece to the tower and making it act also as the distributing plate by providing on its surface a number of inlet holes fitted with an overflow boss. For small liquor feeds, however, this device is somewhat inefficient.

Acid-distributor or Splash Box. The acid-distributor or, as it is sometimes called, the constant-level receiver, is

[1] Fr. Pat. 421,952, 1910.

usually carried on the dome of the tower. In present-day absorption practice it has become a convention to make the capacity of this vessel very small, if storage capacity for circulating acid is provided by the saucer at the base of the tower. This, however, is bad practice, since with such small towers and small feeds of liquid absorbent, the maximum storage capacity is required. The usual type of acid receiver and distributor is shown in Fig. 45.

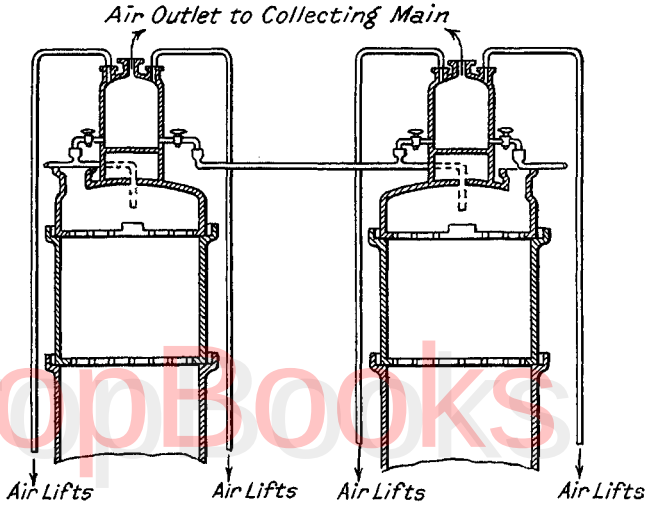

FIG. 45.—Acid Receiver and Distributor.

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These pots are usually 12 inches to 20 inches high and 18 inches to 24 inches internal diameter. Three bosses are provided at the top. Two act as inlets for the air lifts elevating the acid from the base of the tower. The third is connected to a collecting main of about 4 inches diameter, running along the length of the system, which collects all the air from the lifts, which contains nitrous gases and nitric acid. The main is sealed at one end, and the other end is connected into the gas inlet main to the system. The pot is also provided with two (or four) outlet taps, set at the same level. Two of these carry a part of the acid elevated to the next (strongest) tower in the series, while two return the remainder of the acid down the tower again.

Another method of arrangement of these distributing pots is shown in Fig. 46.

One distributor is here effective for two towers and an economy in the number of pottery parts is thereby effected, and also an economy in space.

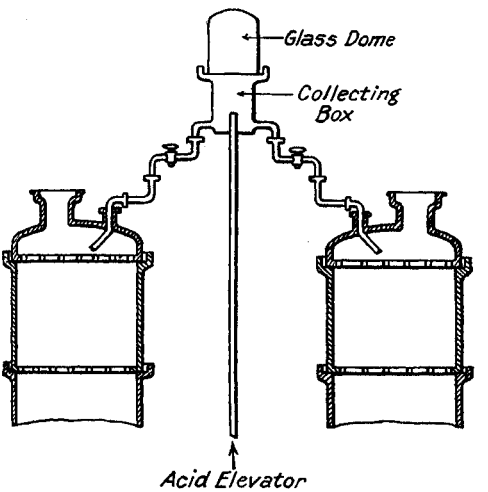

FIG. 46.—Acid Receiver and Distributor.

Gas Mains. The mains conveying the gas from tower to tower vary from 9–15 inches in diameter, and are of stoneware, supported by wooden framework in an exactly similar way to the tower sections. These mains convey the gas from the top of one tower to the bottom of the next.

There are two general methods of connecting the mains to the towers: firstly, those in which the dome piece is made with a socket to take the outlet bend; and secondly, those in which the top section of the tower contains the outlet socket. In these two types of construction the connecting main has two different positions. In the older type of tower with the outlet in the top section, a large amount of valuable oxidation space was lost, and, in addition, the towers had to be spaced more widely apart than in the newer type of construction, in which the connecting pipes are carried out from the dome piece and down the back of the towers.

This latter method effects a greater economy of space than the former.

The towers are operated so that a counter-current principle between gas and liquid is maintained. The gas is drawn through the system under suction, and passes up each tower, and is then carried to the base of the next tower in the series.

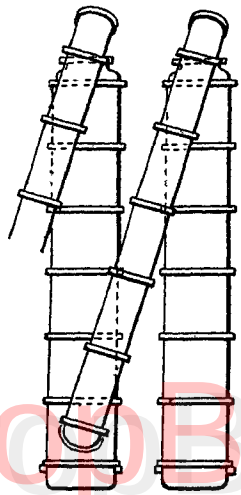

FIG. 47.—Gas Main Connection to Absorption Tower, through Dome.

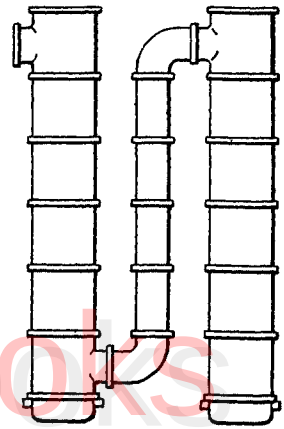

FIG. 48.—Gas Main Connection to Absorption Tower, through side of top section.

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The absorbing liquid, which is usually water, passes down each tower, and is elevated to the top of the next tower in succession, the most concentrated nitric acid being obtained ultimately from the gas-inlet tower.

Removal of Weak Nitric Acid. The acid running from the bottom of the gas-inlet tower is commonly run into an earthenware receiver or " bosh " of approximately 200 gallons capacity standing about 2 feet above ground level, to facilitate the subsequent removal of the acid into carboys for storage or transport. If the weak acid has to be absorbed in another plant cycle, it is usually drawn off from the lifts at the top of the tower and carried by overhead mains to the desired position. The provision of a storage tank at the end of the

system makes it much easier to check the output of the system, and also to secure accurate samples of the acid made.

Size of Absorption Sets. Such towers as have been described are operated in sets of six to eight towers in series. It is inadvisable to work a greater number than this in series, as it entails the handling of a large bulk of dilute nitrous gases in the end towers of the system, combined with a big increase in the suction required owing to the resistance of the packing, air leakage, etc. In addition, the ground space required is more economically utilized and the control and supervision simplified, since gangways, staircases, etc., can be erected economically between the sets of towers, and the acid elevation and distribution system effectively centralized.

Large-type Absorption Towers

The size of stoneware towers is limited by two important factors:—

1. The maximum size of the individual stoneware sections which can be made.

2. The resistance of the material to lateral pressure and also its crushing weight.

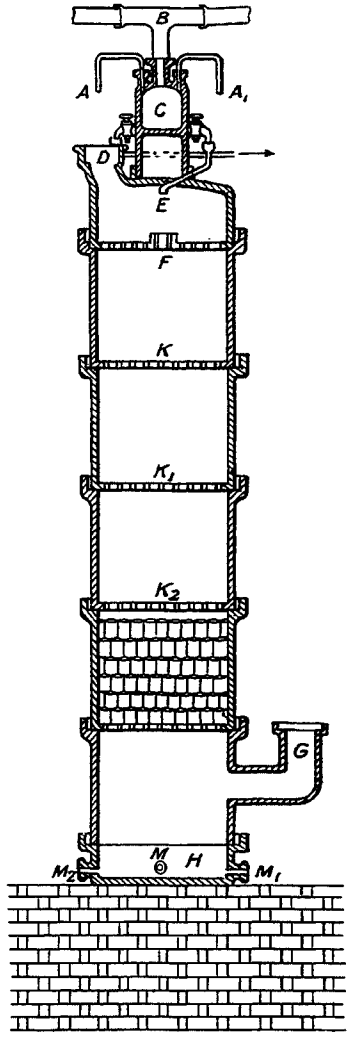

Fig. 49.—Absorption Tower (small-type), Stoneware Sections.

A, A_1, Air Lifts from Base of Tower. B, Collecting Main for Fume from Pohle Lifts. C, Collector and Distributor for Circulating Acid. D, Gas Exit from Tower. E, Water Inlet to Tower. F, Distributing Plate. G, Gas Inlet to Tower. H, Acid Storage Basin for feeding Air Lifts. M, M_1, M_2, Outlet Taps to Air Lifts. K, K_1, K_2, Perforated Slate Slabs to support Packing.

The maximum size of stoneware section which is made at the present time is approximately 4 feet 6 inches diameter and

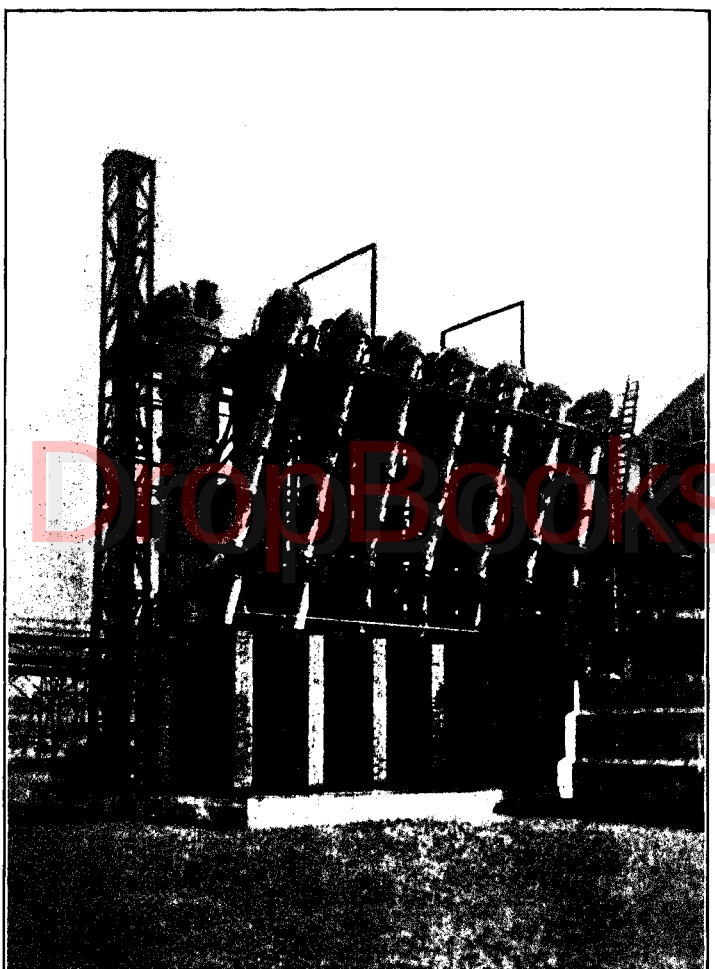

Fig. 50.—Set of Stoneware Absorption Towers.
Technical Records of Explosive Supply, 1915–18, No. I.

4 feet high, and the height to which towers can be constructed with these sections is severely limited by the mechanical disabilities of the material. In addition, such structures

become very costly as the size is increased disproportionately to the increase gained in absorption capacity. The use of stoneware or earthenware towers is consequently limited to comparatively small recoveries of nitrous gases, which are usually in high concentration. A set of eight towers of the type previously described, for example, would yield 25–30 tons of nitric acid (as 100 per cent.) per week of 168 hours, when dealing with a nitrous gas containing 12–15 per cent. NO_2, but with a gas containing only 2 per cent. NO_2 the amount recovered would be less than 2 tons per week.

Where relatively large quantities of dilute nitrous gases have to be handled, therefore, an enormously increased absorption capacity is required. For example, to absorb 1 lb. of NO_2 per minute from a gas containing 15 per cent. NO_2 requires approximately 120–130 cubic feet of tower space, while to effect the same amount of absorption with a gas containing 1 per cent. NO_2 by volume requires more than 5,000 cubic feet. A set of eight small towers recovering 30 tons of nitric acid per week from a gas of the former concentration would need to be enlarged to forty sets to recover the same amount from a gas of the latter composition. The capital cost of the small towers and the enormous ground space required thus prohibit the use of the stoneware tower in the large-scale nitrogen-fixation industries. It is difficult to arrive at a satisfactory ratio of cost per cubic foot of absorption capacity of small stoneware towers as compared with the large-scale brick towers. It may be taken as a rough approximation, however, that ratio of cost per cubic foot of absorption capacity of stoneware towers 3 feet diameter and 15 feet high is at least one and a half times the cost with towers 60–70 feet high and 6–10 feet diameter. The ratio would probably be as 1 : 1·75 under normal conditions of labour and material costs. Since the two essential factors for absorption, other things being equal, are cubic capacity and wetted surface, it is evident that increased height and diameter of units is absolutely necessary for the economic absorption of the large volumes of dilute nitrous gases which are produced in the arc fixation process. In this process, towers of 70–80 feet high and 10–20 feet diameter are commonly used. In ammonia-oxidation processes the towers are usually 50–60 feet high and 6–10 feet diameter. At the

Notodden factory in Norway of the Norwegian Hydro-electric Company 25,000–30,000 cubic feet of gas per minute, containing approximately 1 per cent. by volume of nitric oxide, have to be dealt with. The absorption takes place in three series of five towers, each tower being 70 feet high and 20 feet diameter and of octagonal section. If we consider (as is approximately the case) that the absorption capacities of large and small towers are in direct ratio to their cubic capacities, it can readily be shown that the fifteen large towers used by this company are equivalent to over 4,000 small towers 14 feet high and 3 feet diameter. Similarly at Oppau and Leverkusen, in Germany, synthetic ammonia is catalytically oxidized to oxides of nitrogen, which are absorbed in water. The towers used are (*a*) brick towers 80 feet × 20 feet, (*b*) granite towers 80 feet × 30 feet, and (*c*) steel towers (for alkaline absorbents) 80 feet × 15 feet. Meister Lucius & Brüning at Höchst use similar towers 40 feet high and 20 feet diameter.

Construction Materials. The materials available for the construction of such large towers are limited, as it is desirable to have material which will resist fairly high pressures and which is also unattacked by dilute nitric acid. It is also desirable to reduce the number of joints to a minimum, since they are a potential source of leakage. At Rjuken (Norwegian Hydro-electric Co.) the problem has been solved by building the towers of granite slabs. These are set with the thinnest possible layer of a cement usually consisting of a mixture of sodium silicate and silicious material such as granite dust, asbestos, sand, etc. The inside of the tower is protected by a thick layer of asphalt 3–6 inches thick. Each tower is octagonal in section and is strengthened against the lateral pressure of the packing by tie rods, attached to an external framework surrounding the tower. A similar type of construction is also used in some of the German and American systems.

In England very good acid-resisting bricks are obtainable, e.g. Obsidianite, Nori ware, Duro ware. The cost of construction and probability of leakage, however, with towers built of such bricks, is very considerable, and the difficulty is accentuated by the fact that until quite recently it was almost impossible to obtain a satisfactory cement for the purpose.

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The recent developments in the production of acid-resisting cements, which, while being resistant to acids, can be used with the same ease and certainty as ordinary mortar, has rendered

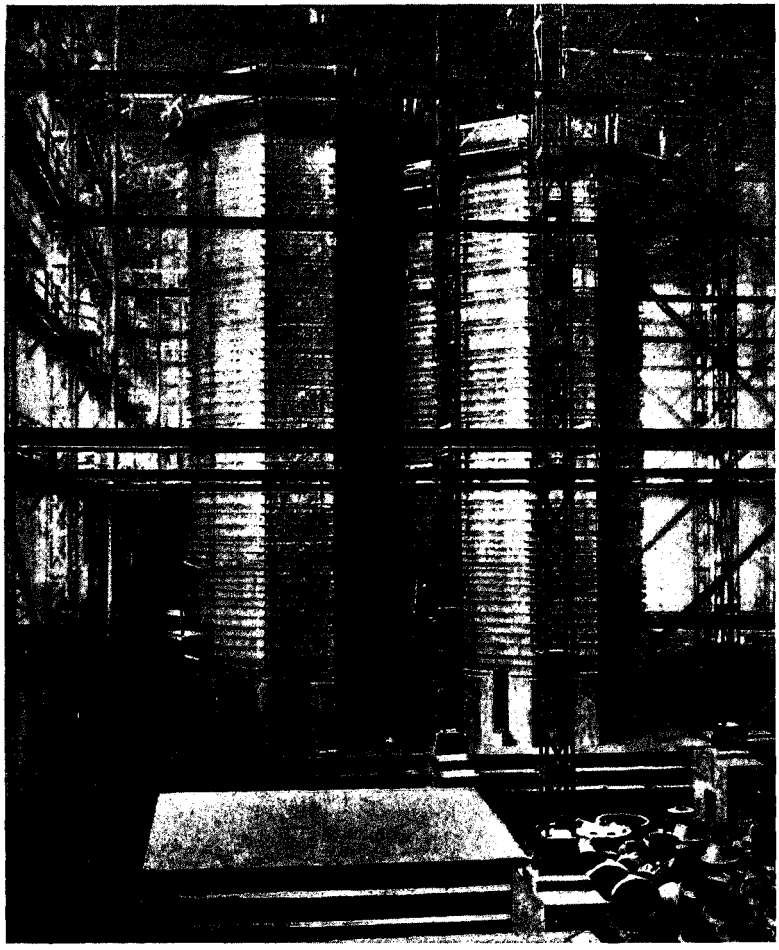

FIG. 51.—Granite Absorption Towers at Rjuken.
Norwegian Hydro-electric Company.

it possible to construct square or circular towers of any reasonable height, using ordinary acid-proof bricks. With such cements, absorption towers of 40–70 feet high have been built

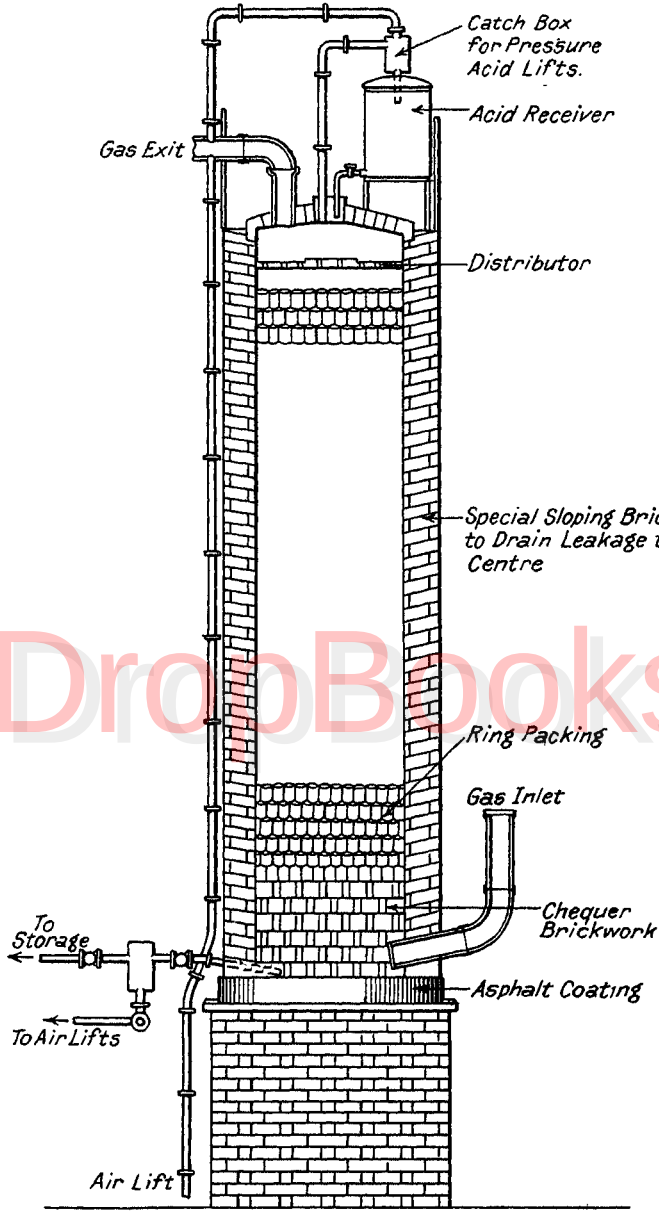

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FIG. 52.—Absorption Towers (large-type).

in less time than if ordinary mortar had been used. The economy in using such a type of construction is obvious. Instead of the haulage and handling of large blocks of stone, towers can be constructed of good acid-resisting brick more easily and more economically. At one English works, two such towers, 70 feet high and 12 feet internal diameter, have been constructed and operated with considerable success, and the further development of the brick tower is only a matter of time.

A special type of brick has also been developed by Messrs. Chance & Hunt, Oldbury, which is designed to prevent the possibility of external leakage (see Figs. 52 and 53). These were made in such a way that the horizontal joints all sloped towards the centre of the tower, and consequently any acid drips would tend to be carried to the inside, and not to the outside, of the tower. The lateral pressure of the packing in such large towers necessitates a considerable thickness of tower wall being used, 3 feet thickness being quite common. In addition, the towers are also provided with iron bands or tie rods bolted at intervals round the circumference.

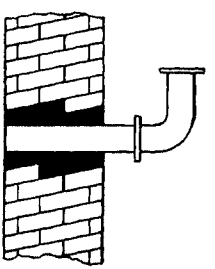

FIG. 53. — Detail of Inlet Pipe Setting.

An example of such a type of tower is shown in the illustrations of the towers of the Norwegian Hydro-electric Co. at their new plant at Rjuken, the towers being built of red granite, 75 feet high and 22 feet external diameter (Fig. 51). A view is also shown of the towers in the air nitrate plant at Muscle Shoals, U.S.A., where bricks laid in acid-resisting cement are used, but the towers are also strengthened by suitable tie rods (Fig. 54). The thickness of tower wall necessary can be decreased by the use of a scientific self-supporting packing material. In one particular case the wall thickness could be reduced from 3 feet to 1 foot 6 inches by such a change in the packing material. The larger tower units are again preferably set on brick or granite piers. The base of the tower is usually given a slight slope for drainage purposes. An internal bedding of asphalt is commonly used.

The general factors governing the distribution of acid and

gas in the larger tower are essentially similar to those in the case of the smaller towers. Acid storage is provided, however, not in the tower itself, but by means of storage tanks placed at the top and bottom of the tower. The elevation of the circulating acid also demands increased capacity of air lifts, eggs, or pumping apparatus.

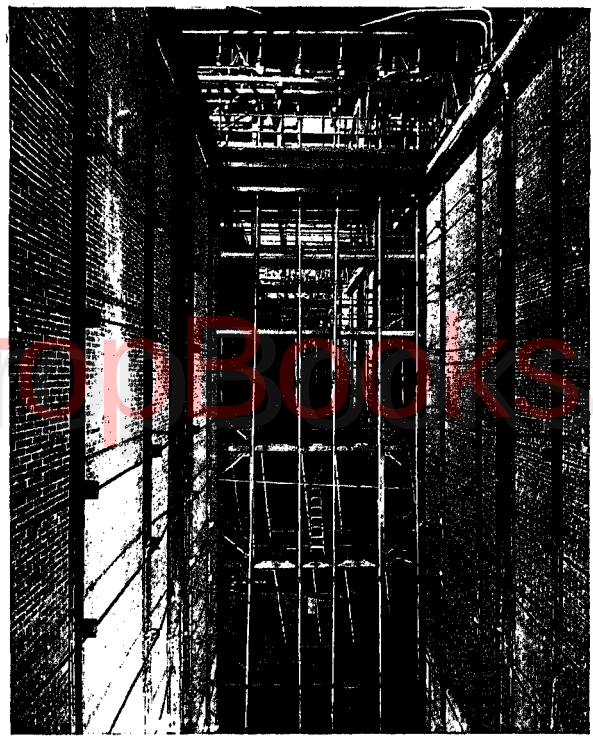

FIG. 54.—Absorption Towers at Air Nitrates Plant, Muscle Shoals, Alabama.
Sullivan Machinery Co.

Acid-distributor. For towers of diameters greater than 3–4 feet, the splash plate and gravity feed are useless and the system of distribution generally adopted is the constant-level overflow type commonly used in the Glover tower in sulphuric acid manufacture. A large number of separate small streams are in this way delivered down the tower. The use of sprays

is also practised in some systems, but if these are of the nozzle or jet type, considerable trouble through choking usually occurs. A type of spray which is very useful for large-diameter towers consists of two horizontal pipes at right-angles, with a number of holes pierced in the sides. These are caused to rotate by the pressure of water fed to them. This type of spray is in use in a number of industries, particularly in the cement industry. The use of the device in absorption practice, however, necessitates the top of the tower being completely enclosed. For even distribution and simplicity of operation this method possesses important advantages, and it is in every way superior to the cumbersome overflow-type of distributor commonly met with in acid manufacture.

The top of the larger-type tower is almost invariably flat, since this allows receiving and storage apparatus to be erected with greater facility, and is also cheaper in initial cost.

In cases where the final absorption of the more dilute nitrous gases is effected by milk of lime or caustic soda, it is possible to construct the absorption towers of wood or iron. There are a number of factors in the design of both large and small towers which require careful consideration before a plant is laid down to deal with a given quantity of nitrogen oxides. Some of these points will now be briefly considered.

Design of Absorption Towers

Shape of Cross Section. The earlier types of large tower for absorbing not only nitrous gases but many other gaseous substances, e.g. hydrochloric acid, were built with square cross section. From the point of view of economy in construction, this shape has undoubted advantages, particularly where the towers are constructed of large blocks 3 feet or so in thickness. Square towers have several disadvantages in absorption practice, however: firstly, in the difficulty of securing even distribution of the gas and liquid over the tower, the corners usually being the cause of considerable loss in efficiency through channelling, etc.; secondly, the corners add considerably to the difficulty in prevention of leakage.

It is generally recognized at the present time that the round tower is the ideal type, and gives the greatest efficiency for its cubic space and wetted surface. While previously the diffi-

culty of securing cheap materials for construction gave the square tower an economic advantage, that difficulty is no longer present, and consequently the round tower is almost universally adopted.

Ratio of Diameter to Height. The shape of cross section of the tower has also a considerable bearing on the ratio of diameter to height, since difficulties of gas and liquid distribution, which may be inconsiderable with a tower of small diameter, are magnified considerably as the diameter of the tower is increased. It is a matter of experience that when an ordinary gravity feed of liquid enters the top of an absorption tower, it is not until a distance of several feet down that the whole of the packing is homogeneously wetted. In consequence, a certain amount of the tower space is not utilized. It is well known also that the wider the tower, the more difficult is it to secure good distribution of the absorbing liquid. Some kind of constant-level overflow apparatus has to be used, with all its cumulative defects due to accumulation of grit and dirt, etc., while in addition it is inevitable that channelling will take place to a very increased extent. This has been the experience of most users of towers of diameter greater than 12–15 feet. Careful consideration should be given, therefore, to the question of limiting the diameter of the tower to a maximum of 10 feet. It is also evident that, even with a good packing, the gas entering the tower at a point in the circumference will be drawn up the tower for some distance before it is spread homogeneously over the tower. The wider the tower, the greater will be the "dead" space so produced.

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For efficient working, therefore, it is advisable that the ratio of $\frac{\text{diameter}}{\text{height}}$ should not exceed $\frac{1}{5}$ to $\frac{1}{6}$. At Notodden the towers are 20 feet diameter and 70 feet high, as already stated. In this connection it should be mentioned that the American nitrate plant at Alabama had absorption towers 60 feet high and 13 feet square for handling approximately 1,600 tons of HNO_3 per week. The Badische Anilin und Soda Fabrik at Oppau and Leverkusen use two brick, two granite, and two steel towers (for alkaline absorbents), 80 feet × 20 feet, 80 feet × 30 feet, and 80 feet × 15 feet respectively, to recover approximately 2,000 tons of HNO_3 per week. Meister Lucius

& Brüning at Höchst, however, have constructed towers 40 feet high and 20 feet external diameter, and in this latter case considerable difficulty is experienced in utilizing the whole cross section efficiently. In fact, at Leverkusen the difficulties of operation were such that the tower was much less efficient for its cubic capacity than the equivalent number of small type towers, and the towers 80 feet × 30 feet had a lower capacity than the towers 80 feet × 20 feet.

In the case of the small stoneware towers, the ratio of diameter to height is sometimes as high as $\frac{1}{1}$, since the difficulty of distribution is not so acute with towers of diameter 3 feet or less. It is a matter of experience that absorption systems in which the ratio is $\frac{1}{3}$ or $\frac{1}{6}$ are more efficient for their cubic capacity and wetted surface. The small towers, therefore, if built of stoneware sections 3 feet diameter and 3 feet high, should contain five sections in each tower.

Other Types of Absorption Towers

A number of variations of what may be called the conventional type of absorption tower have been suggested, some of which are very important. Perhaps the most important is due to Moscicki.[1] The main difference in the absorption tower described in the patent and the ordinary tower is that the passage of the gas is horizontal through layers of very fine quartz 0·1–0·2-centimetre cubes. The earlier type of absorption tower evolved from his experimental work is shown in Figs. 55 and 56. This type of apparatus was put up on an experimental scale at the University of Fribourg. The description of this, as given in Moscicki's article in *Chimie et Industrie*, is briefly as follows:

Each tower is composed of two segments, the lower functioning as the true absorption chamber, the upper being empty, and functioning as an oxidation chamber.

The absorption chamber proper consists of two concentric cylinders A and B (Fig. 55). The space between the tubes A and B is filled in the upper part with very small fragments of quartz and in the lower part with slightly larger pieces. Both A and B are pierced with inclined holes approximately

[1] Eng. Pat. 17,355, 1911. His work is described in detail in *Chimie et Industrie*, Vol. **2**, Nos. 11 and 12, Nov.–Dec., 1919.

1 cm. diameter, evenly disposed over the surface. The opening D on the outer vessel C serves as an exit for the gas. E and F are liquor outlets. Two outlets are provided lower down for feeding the air lifts.

The lower vessel is hermetically sealed by the dome H placed in the socket G. The dome H carries two inlets, K and J.

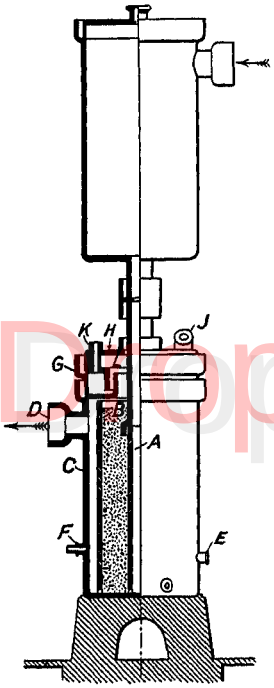

FIG. 55.—Section of Moscicki Experimental Absorption Tower.

Chim. et Ind., 1919, Vol. 2, Nos. 11 and 12.

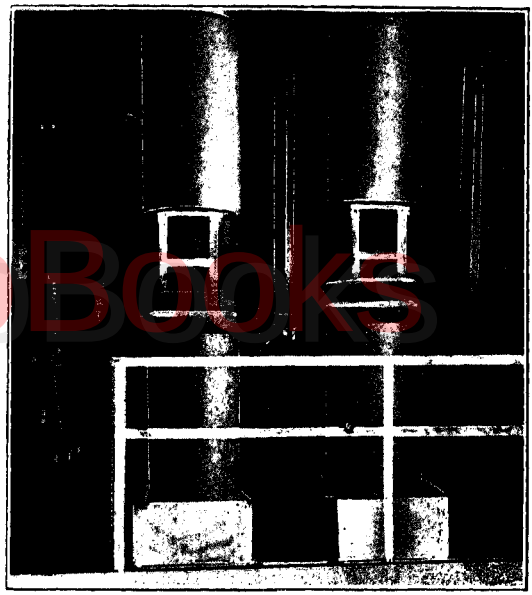

FIG. 56.—Moscicki Experimental Absorption Towers at Fribourg.

Chim. et Ind., 1919, Vol. 2, Nos. 11 and 12.

The inlet J serves for the introduction of the liquid absorbent. K is connected to a compressed-air supply, and distributes the absorbent round the tower in the annular space L, formed between the socket G and the dome H. The gas enters into the upper empty section, and there the nitric oxide is oxidized. The gas then passes down the pipe A, then through the oblique openings in B, traversing B horizontally. It then passes out

of B into the annular space formed by B and the outer vessel C, and from thence out by D to the next tower.

The tower has since been considerably enlarged by Moscicki for the Société anonyme pour l'Industrie de l'Aluminium at Chippis in Switzerland.

Fig. 57 shows the type of tower system finally described in Moscicki's patent (1911). The chamber is divided into a series of smaller compartments by perforated partitions. These chambers are filled to a certain height with quartz, and alternate chambers may act as oxidation chambers.

The system is essentially counter-current, the gas passing

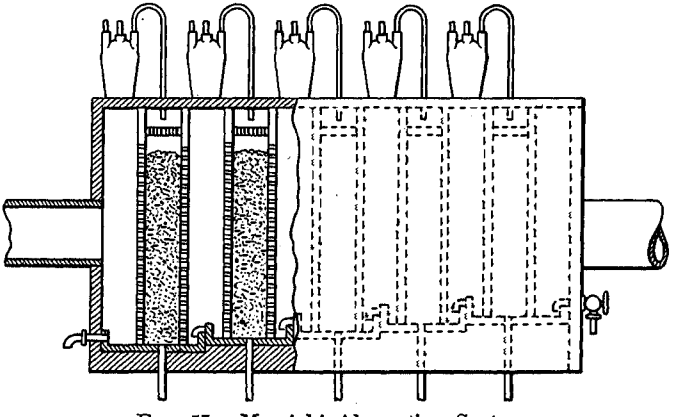

FIG. 57.—Moscicki Absorption System.
Chim. et Ind., 1919, Nos. 11 and 12.

along horizontally and the liquid falling vertically but being carried on to successive towers in a direction opposite to the flow of the gas.

The main advantages claimed by Moscicki for his towers are as follows:—

1. The use of very finely divided filling material giving a maximum surface.

2. Considerable amounts of liquid may be circulated down the towers, without increasing materially the resistance to the passage of the gas.

Of these, the advantage 2 is the more important; 1 is considered in the chapter on packing materials.

If the question of horizontal flow of gas is disregarded, the

Moscicki system differs from the modern type of tower in that the latter is designed to give both oxidation space and high absorbing surface in the same tower, while the former system alternates very closely packed, high scrubbing space, with oxidation chambers. Although the use of such fine-grained quartz as a filling material brings in train troubles due to resistance to gas passage and to high lateral pressures, the alternation of absorbing space and oxidation space has some points of attraction. It must be emphasized, however, that the capacity of the system will be mainly governed by the longest "time" reaction, viz. the oxidation of nitric oxide, and it does not follow that, even if the regenerated nitric oxide is given sufficient time to oxidize completely to nitrogen tetroxide between each water absorption, the capacity of the system is thereby increased, although the efficiency might be improved.

A number of proposals have also been made to spray the liquid absorbent into unpacked towers through which the gas is passing. Fig. 58 shows the proposals of Dawson [1] in this connection. The liquid absorbent is introduced at the bottom of the tower, and a jet of air J, inside a funnel F provided with holes at its base, and of which the upper part is above the liquid level in the tower, throws up a fine spray of water in the same direction as the gas. The towers are in series. The gas passes from G to G_1 and the liquid from L to L_1.

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Such processes are obviously uneconomical, since the volume of liquid which can be sprayed is only a fraction of the volume of the gas passing through, and consequently the amount of contact between gas and liquid molecules will be much less than if the gas were passed through a packed tower containing a considerable amount of wetted surface. A United States Patent [2] proposes that in the ordinary tower system each tower should be provided with its own circulating pump, and that while the gas flows in the same general direction as the liquid, it should pass up one tower and down the next, and so on through the series. A somewhat similar suggestion is made in Eng. Pat. 120,378, 1918, in which it is proposed to cause the oxygen required for the absorption to move counter-current to the liquid as a whole, but in the same direction as the liquid

[1] Eng. Pat. 120,869, 1918. [2] U.S. Pat. 1,314,802, 1919.

in the separate parts of the apparatus, the advantage claimed being that a circulation of liquid is established thereby, and prolonged contact of gas and the liquid obtained. In addition, other patents describe the alternation of oxidation towers with absorption towers. This point was discussed in Chapter II.

Up to the present, it is quite apparent that these modifications of the ordinary water-absorption system have not been developed to any extent in large-scale practice, except in the case of the Mosciçki system, which appears to give good

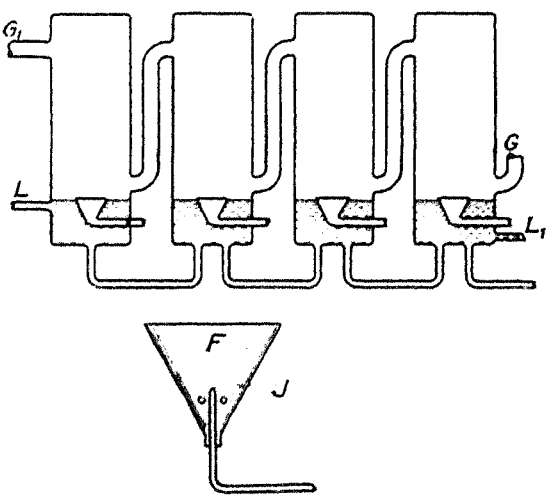

FIG. 58. Unpacked Absorption Towers.
R. Dawson, Eng. Pat. 120,869, Sept. 1918.

results. The provision of a large amount of scrubbing surface and, at the same time, a big proportion of oxidation space, in the most economical manner, is the crux of the whole matter. It will be seen from the descriptions previously given that the attempts at the solution of this problem are only two: firstly, the alternation of heavily packed (i.e. high-surface) towers, with empty oxidation towers; or the distribution of scrubbing surface and unpacked space in one and the same tower. The latter type of tower predominates, owing chiefly to the fact, already stated, that if it is attempted to oxidize nitric oxide much beyond the stage represented by N_2O_3, a much longer

time is required and the capacity of the system tends to become less.

Cost of Absorption Systems

The capital cost of an absorption system is one of the heaviest items in a nitrogen-fixation plant, and indeed wherever nitrous gases have to be recovered. Very large cubic capacities are required for the ordinary absorption by water, and the gross tower space required increases considerably as the available concentration of nitrous gases becomes less. The costs of systems may be conveniently divided under two heads: the small stoneware systems dealing with concentrated nitrous gases, and the larger systems handling dilute gases.

Small Stoneware Systems. It is a matter of practical experience that approximately 120–130 cubic feet of tower space is required to deal with 1 lb. of nitrogen tetroxide per minute when contained in a gas containing 10–15 per cent. NO_2 by volume. If we assume that a scientific packing material is used, giving 70 per cent. free space, the free space required for 1 lb. of NO_2 per minute would be about 90 cubic feet.

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Since 1 lb. of NO_2 per minute corresponds to approximately 6 tons of nitric acid (as 100 per cent.) per week, we can take as a basic figure that the recovery of 1 ton of nitric acid (as 100 per cent.) per week requires 25 cubic feet of gross tower space when dealing with a gas containing 10–15 per cent. NO_2 by volume, and using a packing material giving 70 per cent. free space.

The average size of the small absorption tower may be taken as 3 feet diameter and 13 feet high, disregarding the volume occupied by accessory fittings. This gives approximately 90 cubic feet of gross tower space in each tower. Each tower of these dimensions therefore corresponds to a recovery of 3·6 tons of nitric acid (as 100 per cent.) per week. The cost of erection of a set of eight such towers at the present time is about £2,000, which gives a capital cost of approximately £70 per ton of nitric acid (as 100 per cent.) per week. This figure must be taken as being an extreme maximum, since prior to 1914 the figure approximated more closely to £40 per long ton (2,240 lb.) of nitric acid per week for small installa-

tions, which is rather less than £1 per ton of nitric acid (as 100 per cent.) per annum.

Large-scale Systems. With increase in the cubic capacity of the tower systems, it should be possible to reduce very considerably the capital expenditure per unit of fixed nitrogen, but the increased dilution of nitrous gases to be handled requires a much greater gross absorption capacity, and consequently much increased capital cost. The results obtained from Norwegian practice and from continental ammonia-oxidation plants indicate that the capital cost for an absorption section is approximately £2·5 per metric ton (2,200 lb.) of nitric acid (as 100 per cent.) per annum.

The arc process at Chippis, erected under the Moscicki system, is stated to have cost £68,000 to £72,000, exclusive of the power section and fittings.

The cost of the absorption system in this installation was approximately £2·83 per metric ton HNO_3 per annum, and it is considered that this may be taken as a fair working basis for the large-scale absorption systems.

It is probable that the capital cost of absorption plant will be considerably reduced when the water-absorption system can be replaced by alkaline absorption. At present it forms a very costly item in the fixation plant, amounting often to 45-50 per cent. of the total cost of the installation.

CHAPTER IV

FILLING MATERIAL FOR ABSORPTION TOWERS

Before much scientific consideration was given to the question of filling absorption towers, it was the common practice to fill them in a haphazard manner with the cheapest available material, e.g. quartz, broken bricks, glass, granite, coke, and so on. The tower was then in use without attention for long periods, and usually with very inefficient results. Of these materials, those which have persisted are mainly broken quartz and coke. The latter is still used considerably in Gay-Lussac towers, while broken quartz was also largely used, and is still in use, in the absorption towers at Notodden and Rjuken.

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Before discussing the advantages and disadvantages of these filling materials, it is important to define the functions which should be fulfilled by a good packing material. It must be emphasized that the absorption of nitrous gases differs in several important respects from the simple solution of a gas in water. The latter is only one of the reactions taking place in an absorption system. After the solution of the nitrogen tetroxide, there occurs its reaction with water, producing nitrous and nitric acids; then the decomposition of the nitrous acid, with the production of nitric oxide; and finally the oxidation of this latter gas to nitrogen tetroxide by atmospheric oxygen. Apart from the amount of wetted surface given by the filling material, therefore, the suitability of the material for promoting gas mixing and oxidation must also be considered.

Peterson [1] states that a good packing material should fulfil the following conditions:—

1. The opening between the packing sections should be as small as possible, to ensure that the cross section shall be effective.

[1] *Zeitsch. angew. Chem.*, 1911, **24**, 972.

2. For the avoidance of dust and slimy deposits, broad faces and hollows on the upper side of the material should be avoided.

While these points are important, they do not represent by any means the whole of the functions of the filling material used in absorption towers for nitrous gases. Consider the points in tower construction and operation, on which the filling material has an important bearing. These are defined very clearly by Nielsen [1] as follows :—

1. The "free" or reaction space and its influence on the size of the tower.
2. The effective scrubbing or contact surface.
3. The distributing action of the material with respect to both gas and liquid, which also includes the capillary effect.
4. The resistance to the passage of the gas.
5. The amount of liquid retained in the tower, i.e. drainage of packing.
6. The symmetry of the packing with respect to the shape of the tower.
7. The ease of filling and quantity of packing required.
8. The weight of the packing, especially in its effect in producing lateral pressure on the sides of the tower.
9. The chemical action of nitric acid on the material.
10. Cost of filling material and labour of filling—

to which may also be added the liability of the material to cause choking by grit, etc.

Before considering these points in detail, some of the more common types of filling will be described. Absorption-tower filling or packing may be divided into two main types: (*a*) Symmetrical packing; (*b*) Random packing. The terms are almost self-explanatory. Symmetrical packings are such that they can readily be arranged in the tower to form a symmetrical arrangement. A random packing is one which is not capable of symmetrical arrangement in the tower, but which may yet fill the tower more or less homogeneously.

Symmetrical Packings

Ring Packing. This packing consists of cylinders of acid-resisting, unglazed, siliceous material made in various

[1] *Chem. Trade J.*, May, 1914.

sizes to suit different diameters and heights of absorption towers. A common size is 4 inches diameter, 4 inches high and $\frac{1}{4}$–$\frac{3}{8}$ inch thick. These are packed into the tower as shown in Fig. 59 and divide the tower into a number of small hollow tubes of irregular path.

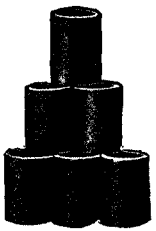

FIG. 59.—Ring Packing.
Oates & Green, Ltd.

Various modifications of the simple ring or cylinder packing exist, which are designed in the main either to secure greater mixing effect when the gases pass through them, or else to give greater scrubbing surface. The majority of these modifications usually possess an addition to the hollow core of the ring. A number of these are shown in Fig. 60.

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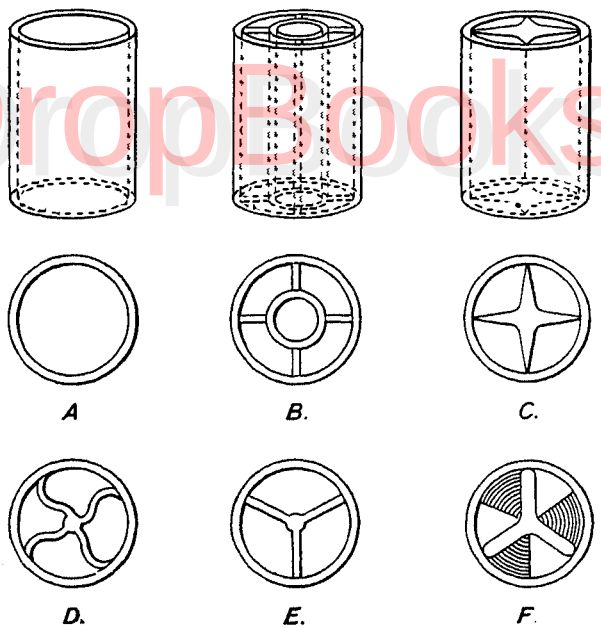

FIG. 60.—Filling Material for Absorption Towers.

A, Plain Ring Packing (4 inch × 3 inch). *B*, Concentric Ring. *C*, Ring and Star (one type). *D*, *E*, *F*, Plan of Ring Packing containing various centre fillings such as Blades (*D*), Triangular Pieces (*E*), and Spiral (*F*).

For example, a concentric ring may be added, or a star-shaped piece which forms a loose fitting. This latter type of

filling material is known as "ring and star" packing. Alternatively, the star may be replaced by a spiral, which may be made in one piece with the outer shell (see also Fig. 61).

In addition, there are types in which the central portion consists of a single plate, crossed plates, or triangular pieces. All these devices are but slight modifications of the cylinder filling. It should be emphasized here that the use of loose pieces in a cylinder packing greatly increases the difficulty, and consequently the cost, of packing an absorption tower.

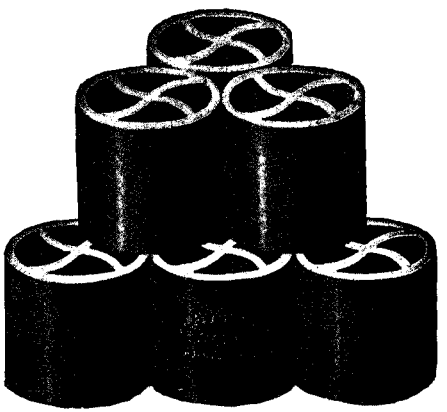

FIG. 61.—Absorption-tower Filling.
Maurice A. Knight.

Modifications of cylinder packing have also been put forward in which the shell itself is distorted. Such a filling material

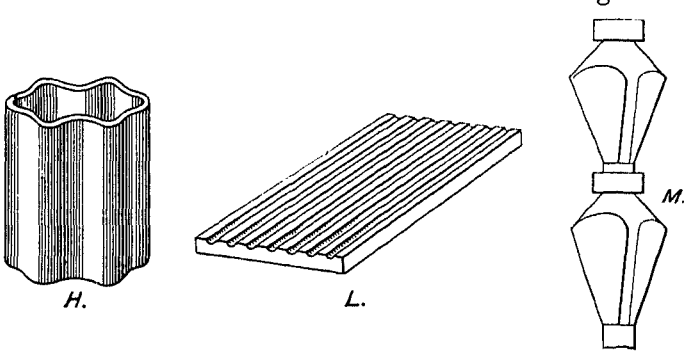

FIG. 62.—Filling Material for Absorption Towers.
H, Crinkled Ring. *L*, Grooved Tile. *M*, Patent Cone-shaped Packing.

is shown for example in Fig. 62 (H). In Fig. 63 is shown a very robust type of filling material suitable for use in high towers where the "crushing weight" of the filling is important.

Propeller Packing and Nielsen Packing. An ingenious

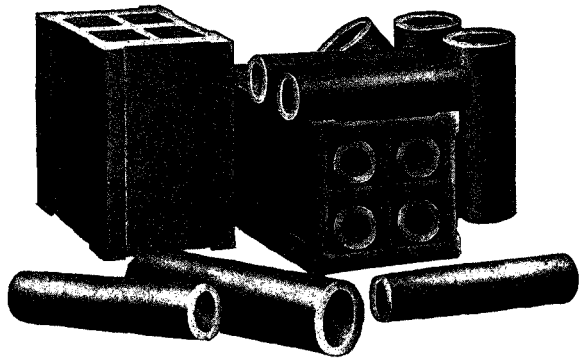

FIG. 63.—Tower Packing.
Maurice A. Knight.

type of filling material which in the author's opinion represents a distinct advance in tower fillings is described by Nielsen.[1] The earlier form of this filling material is shown in Fig. 64. The element consisted of three helical blades with finely corrugated surfaces, and was so shaped that it formed part of a hexagon, as will be seen from Fig. 64 (B), which shows some of the elements packed in a tower. This filling material has been further modified by Nielsen, and while the intrinsic idea of the filling has been preserved, the obvious advantage of using a hollow shell has been introduced (Fig. 65).

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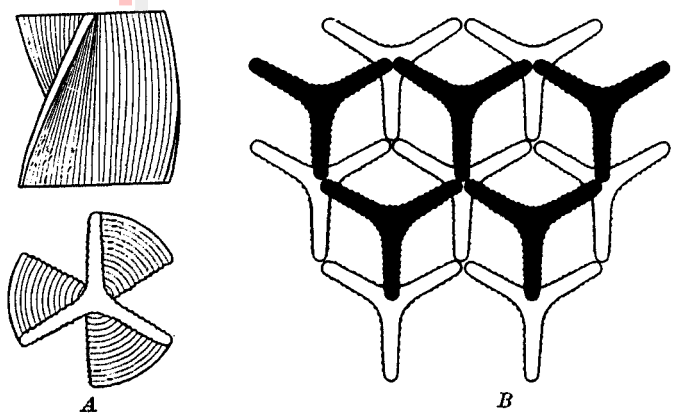


FIG. 64.—Nielsen's Blade Type of Propeller Packing.
A, Element. *B*, Plan of Packing.
John Statham & Sons.

[1] Eng. Pat. 26,269, 1913.

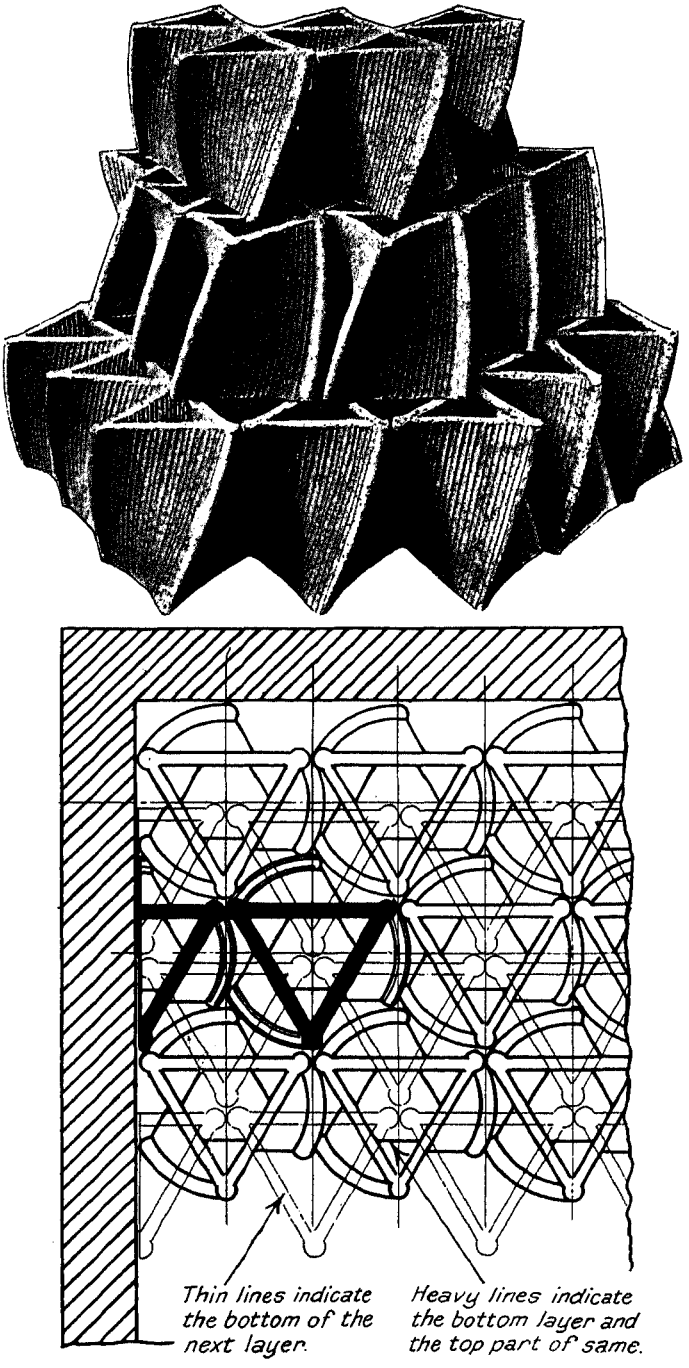


FIG. 65.—Nielsen's New Propeller Type of Packing.
Top, View of Elements. *Bottom*, Plan of Packed Tower.
John Statham & Sons.

The filling overcomes one very important defect of the plain cylinder packing, a defect possessed by several other packings giving a high free space, viz. the tendency of the gas to "streak" through the packing without mixing. In this design, however, the gas is given a whirling motion by its own momentum in passing through the packing.

Guttmann Ball Packing. This type of filling material, first suggested by Guttmann,[1] consists of hollow earthenware balls of vitrified stoneware, approximately 3 inches diameter

FIG. 66.—Ball Filling for Absorption Towers.
Maurice A. Knight.

and $\frac{1}{4}$ inch thick. The balls are pierced with a number of holes $\frac{1}{2}$ inch diameter, symmetrically distributed over the surface (Fig. 66). The balls are laid symmetrically in the tower. This filling material has a number of obvious advantages, and has been largely used throughout the nitric acid industry in this country. It possesses a high "free" space, and when evenly packed causes a fairly homogeneous distribution of gas and liquid. The great disadvantages of the filling lie in its relatively high cost, the tendency to choke if used with dusty gases or gritty liquids, and the low crushing strength, these defects prohibiting its use in very large towers.

[1] *J. Soc. Chem. Ind.*, 1898, 994.

Tile or Plate Packing. Grooved tiles or plates, often pierced with a number of fine holes, have been frequently used as a filling material for absorption towers. They may be constructed of plate glass, hardwood, stoneware, or one of the various iron-silicon alloys (see Fig. 62 (L)). Glass-plate filling, for example, usually consists of pieces of plate glass $\frac{1}{4}$ inch to $\frac{3}{8}$ inch thick, with corrugations on two surfaces. It is packed into the tower so that the corrugations are vertical and parallel with the flow of the gas. The wood and stoneware types vary widely in size, but the ordinary size is approximately 9 inches $\times$ 6 inches $\times$ $\frac{3}{4}$ inch. In a recent patent channelled packing blocks are described which are so arranged that long, narrow, inclined passages are produced, which are inclined at a small angle to the direction of flow of the gas.[1]

In addition to the comparatively simple types already described, there are a number of symmetrical filling materials, some of which are ingeniously designed, but many of which possess a more or less complicated or fragile structure. One of these,[2] for example, describes a hollow filling material, provided with lateral slots (see Fig. 62 (M)), the base of one element fitting into the top of the one below. The disadvantages of such a filling from the point of view of liquid distribution are quite apparent. The element would also be relatively expensive and require skilled labour to pack a tower satisfactorily with it.

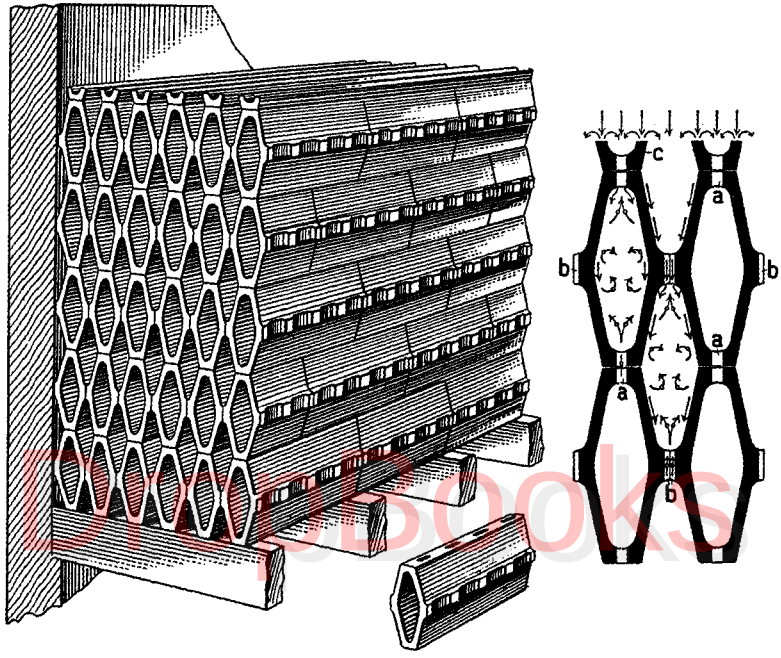
A rather better type of filling, which slightly resembles the above, is Guttmann cell packing, which is claimed to be superior to his ball packing, but which, in the author's opinion, is not nearly so good. The "free" space claimed for this filling is 71 per cent. (as a maximum), and the scrubbing surface 15 square feet per cubic foot (gross).

The cells are made of good acid-resisting stoneware of the shape shown in Fig. 69, and the walls of the cell are provided with horizontal grooves. The top and bottom walls are provided with slots, and on the outside wall are fixed projections, which, with those of an adjacent cell, form the top and bottom slots of the cell formed by four cells in packing.

In Ger. Pat. 229,999, 1909, is described a very complicated type of filling which consists of a cubic framework of siliceous

[1] Eng. Pat. 8,152, 1915. [2] Eng. Pat. 109,915, 1917.

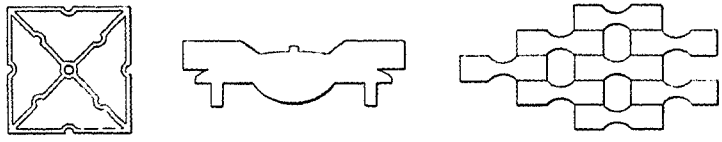
material. Fig. 68 (A) shows one of the six sides of the cube (which are all identical), the length of the side being approxi-



A *B*

FIG. 67.—Guttmann Cell Packing.
A, Arrangement in Tower. *B*, Section of Units, showing Gas Circulation.
Heinz, *Chem. Trade J.*, July, 1913.

mately 4 inches. An English Patent [1] protects a packing having a circular or polygonal central portion with a curved surface,



A. *B.* *C.*

FIG. 68.—Filling Material for Absorption Towers.

provided both above and below with projecting radial ribs or bearers (Fig. 68 B), while another [2] describes a flat, circular

[1] Eng. Pat. 18,831, 1908. [2] Eng. Pat. 12,841, 1899.

filling material, provided with grooved hollows on the upper and lower sides (Fig. 68 (C)).

It is fairly evident that the cost of these filling materials, combined with their lack of obvious advantages over simpler types of filling, will militate against their use in absorption towers for nitrous gases. This is particularly the case with the filling shown in Fig. 68 (A), as it is evident that a structure of this design would be very fragile and costly.

Random Packing Materials

The types of random fillings on the market at present are quite as numerous as those of symmetrical packings. The commonest examples of random packings are materials such as coke, quartz, granite, glass, broken brick, etc., etc.

Coke. This substance was very commonly used in absorption towers for nitrous gases until quite recent years. Pieces of hard coke varying in size from 1 inch to 6 inches in diameter are used, the average size of lump for a small (3 feet diameter) tower being approximately 2 inches $\times$ 2 inches $\times$ 2 inches. The material is thrown in the tower as evenly as possible, the finer material (if different grades are used) being laid at the top.

Quartz. This material is still used to a considerable extent in absorption practice, particularly in countries where stoneware is costly. It is graded in size for tower filling, varying from $\frac{1}{2}$ inch to 2 inches diameter. A similar practice is also followed with broken brick, glass, etc., the material in each case being thrown into the tower as evenly as possible.

Raschig's Elements.[1] This filling consists of elements which may be cylindrical with either one or both ends inclined to an axis, or with ends in the form of a screw, or conical bodies with inclined ends, etc., etc. The elements are made of acid-resisting stoneware and are piled loosely in the tower as homogeneously as possible. This type of filling is perhaps the most commendable of the random fillings at present in use, and the elements are in use in a number of absorption systems at the present time.

There are, in addition to the symmetrical and random fillings already described, a large number of others of varying merit.

[1] D.R.P. 297,379, 1916.

The examples given, however, cover the best types of such materials at present on the market, and it is not proposed to discuss in detail the almost innumerable and often unnecessary modifications of them which have been proposed from time to time.

In order to arrive at a decision concerning the most advantageous type of packing, taking into consideration efficiency and economy, it is necessary to examine each type on the lines of the criteria laid down on page 181. The main differences between the symmetrical and random types of packing are as follows :—

1. Random packing usually causes considerably greater lateral pressure on the sides of the tower. This necessitates very thick tower walls and, in addition, iron strengthening bands at suitable intervals. With symmetrical packing each row takes its share of the total weight of the packing and the lateral pressure is almost negligible.

2. The cost of labour in packing is usually less in the case of random packing, since it can be done by unskilled labourers at a slightly quicker rate.

3. Random packing almost invariably offers greater resistance to the passage of gas than does a symmetrical packing, and with the latter there is also obtained a more systematic distribution of gas.

Apart from these general preliminary considerations, therefore, it will be as well now to consider in detail the points in the construction and operation of absorption towers for nitrous gases, on which the packing material has an important bearing.

Functions of the Filling Material

"Free" or Reaction Space and Scrubbing Surface. It has already been stated in Chapter II that the factor of time is important in the oxidation of the continuously regenerated nitric oxide produced in the absorption system. It is quite evident, therefore, that a sufficient time of passage of the gas through the tower can only be obtained in two ways :—

(*a*) By making the unpacked space (i.e. "free space") as large as possible.

(*b*) By reducing the velocity of the gas.

The velocity of the gas cannot be brought down lower than the rate at which nitrous gases are supplied to the absorption system. It is consequently important that the free space in the tower should be a maximum, consistent with a sufficient area of wetted surface to take up the nitrogen tetroxide formed. The free space and wetted surface will obviously determine the capacity of the system in reference to a given quantity of nitrous gases. They are hence the factors which determine the size of the absorption-tower system for a given amount of recovery. Finally, the free space determines largely the linear velocity of the gas through the system.

The free space given by most packings can be simply and

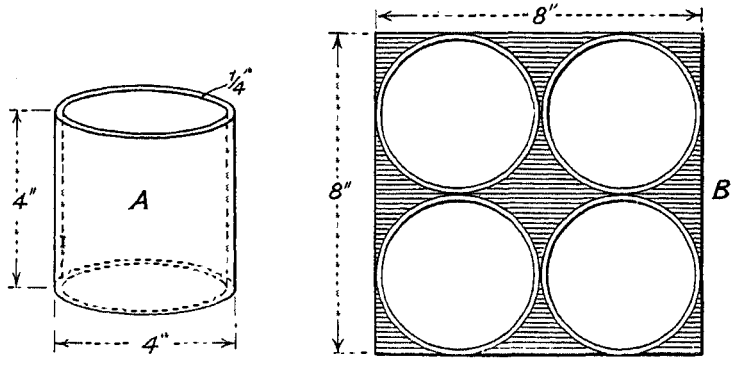


FIG. 69.

approximately measured by finding the amount of water displaced from a cylindrical vessel of known volume, by packing it under standard conditions with the packing to be tested. It can readily be shown by this means that coke packing gives only 25–30 per cent. free space, while quartz (2 inches × 1 inch × 1 inch) gives approximately 40 per cent. On the other hand, there are a number of symmetrical packings which give a free space of 70 per cent. to 80 per cent., and which have at the same time a scrubbing surface of greater area than either quartz or coke.

Such types of packing include ring packing, Nielsen propeller, and Guttmann ball packing, all of which have a high free space combined with scrubbing surface.

Consider a packing of the type shown in Fig. 69 (A).

$$\text{Volume of shell} = \frac{3{\cdot}14 \times \{4^2 - (3{\cdot}5)^2\}}{4} \times 4$$

$$= 11{\cdot}8 \text{ cubic inches.}$$

Total volume enclosed
by packing $= 3{\cdot}14 \times 2^2 \times 4 = 50{\cdot}24$ cubic inches.
$\therefore$ Free space $= 76{\cdot}5$ per cent. (approximately).

This free space is actually larger in practice. In the above calculation only a single element was considered, but in a tower the elements are so packed that a certain amount of unpacked space is enclosed by the curvature of the material when packed (see Fig. 69 (B)). Consider a set of four elements which are contained in a space 8 inches $\times$ 8 inches $\times$ 4 inches.

Total volume occupied by system $= 8 \times 8 \times 4 = 256$ cubic inches.

Total filled space $= 11{\cdot}8 \times 4 = 47{\cdot}2$ cubic inches,
Giving 81·5 per cent. free space.

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Scrubbing Surface. Considering the case of the four rings packed as in Fig. 69 (B) and neglecting the edges which can be assumed to be unavailable as contact surfaces,

Total surface $= 3{\cdot}14 \times (4 + 3{\cdot}5) \times 4 \times 4$ sqnare inches
$= 378$ square inches.

Total volume of packed space (as before) $= 256$ cubic inches.

Square feet of scrubbing surface per cubic foot of packed space $= 18$ square feet (approximately).

As was previously stated, the free space for a coke packing is 25–30 per cent. of the total packed space, while, with broken quartz, the figure is nearer 40 per cent. Consider, furthermore, the scrubbing surface of such packings as quartz and coke. Assume also that the pieces of each are on an average 2 inches $\times$ 2 inches $\times$ 2 inches, and assume that both types of packing give 35 per cent. free space. In practice the material is thrown into the tower at random, consequently several of the surfaces of each piece are rendered ineffective owing to close contact with adjacent pieces. Let us assume, therefore, that the pieces are effective for scrubbing on their vertical sides only, an assumption which is approximately correct.

Number of pieces in 1 cubic foot packed space, assuming 35 per cent. free space, $= \frac{65}{100} \times \frac{1,728}{8} = 140{\cdot}4$.

Four sides of each of these pieces are effective. Each side is 2 inches $\times$ 2 inches.

$\therefore$ Total scrubbing surface
per cubic foot $= 16 \times 140{\cdot}4$ square inches.
$= 15{\cdot}6$ square feet.

In the case of coke packing, this figure would be actually much larger at first owing to the porous nature of the material, but it is well known that such pores in hard coke become rapidly clogged with dust or by the capillary action of the acid. In addition, even in the cold, reduction of nitric acid takes place, with consequent disintegration of the coke and further choking up of the gas and liquid passages. The figure obtained for the scrubbing surface available in practice is therefore quite a fair one. It is thus clear that coke and quartz packings give only one-half to one-third the free space of a packing such as stoneware rings, and the scrubbing surface is also much less. The towers therefore have to be increased in the proportion of the relative free space and scrubbing surface to give the same capacity. The apparent economy in coke and broken quartz packing is thus far outweighed by the increase in cost of construction of the towers and the increased ground space required.

The modifications in ring packing, such as the ring and star, and ring and spiral types, increase the scrubbing surface of the packing at the expense of the free space, and also aim at securing more efficient mixing of the gases. While the amount of scrubbing surface is an important factor, it is usually the case that the scrubbing surface is sufficient with most types of packing, and that the ultimate loss of nitrogen occurs as nitric oxide, i.e. the time of the gases in the towers has been insufficient. It is therefore inadvisable to cut down the free space of the packing merely to increase the scrubbing surface.

There are a number of other types of packing which also give a high free space combined with scrubbing surface. Of these the most important are Nielsen propeller packing and

Guttmann ball packing. Table 31 [1] shows the relative free space and scrubbing surface obtained with the types of packing previously described.

TABLE 31

Packing.	Scrubbing Surface sq. ft. per gross cubic ft.	Free Space, i.e. percentage gross Space not occupied by Packing.
Ring packing (4″ × 4″) . . .	18·0	81·5
,, ,, with star . . .	28·5	66·0
,, ,, with concentric ring	30·0	67·0
Nielsen propeller (solid type) . .	25·8	77·5
,, ,, (hollow type, 4″ × 4″)	22·5	80
Coke (2″ × 2″ × 2″)	15·0	25–30
Granite	16·0	35–40
Guttmann ball packing . . .	25·0	88·0
Guttmann cell packing . . .	15·0	71·0

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It will be seen from these figures that a scientifically designed packing has a tremendous advantage over the old type of random packings, such as coke and quartz. This advantage is also maintained when the question of the resistance of the packing material to the passage of the gas is considered. Both coke and quartz are disintegrated to some extent by nitric acid, and consequently quantities of fine material are produced which clog up the gas passages to such an extent that ultimately the tower becomes completely blocked. So far as the scientific packings themselves are concerned, there is not very much difference between them. Guttmann cells have probably the greatest resistance to gas passage, while the plain ring packing has the least.

Zeisberg (*l.c.*) has obtained an empirical expression for the resistance of packing material to the flow of gas by measurement of the pressure resistance of various packings in a

[1] A table of such values for various types of packing is also given by Zeisberg (*Met. and Chem. Eng.*, 1919, **21**).

tower 2 feet 6 inches diameter and 30 feet high. The expression obtained was

$$p = \frac{kfhv^2s}{a^2}$$

where

p = pressure in inches of water.
s = linear velocity of gas in feet per minute.
k = a fractional constant.
a = area of cross section of packing in square feet.
h = height of packing in feet.
v = volume of air passing in cubic feet per minute.
f = frictional coefficient of 1 square foot of packing, 1 foot high. This must be determined for each material and for each method of packing, i.e. dumped, stacked, or packed symmetrically.

Distributing Action and Capillary Effect. Once the absorbing liquid has commenced its travel down the tower, it is essential that it should be distributed as evenly as possible over the packing. The homogeneity with which this distribution is effected will depend almost entirely on the type of packing used. If the packing is not such as will cause this distribution it will be useless for absorption towers. This point is sometimes lost sight of, and only the free space and scrubbing surface of any particular type of packing taken into consideration. Surface tension or capillary action plays a very important part in this liquor distribution, and may act in two ways :—

(*a*) By causing the films of liquid to converge into a series of relatively flooded channels.

(*b*) By causing the absorbing liquid to spread out over flat surfaces.

It is necessary to consider, therefore, the types of structure in packing which will tend to encourage the effect (*a*) above of capillary action, and those which tend to promote the effect (*b*), and furthermore, those types which tend to cause the absorbing liquid to drop in small streams or drops on to the lower layers of packing, and those which cause it to spread by surface contact. It is evident that if the tower were filled with very fine homogeneous particles of a non-porous nature the

distribution of the absorbing liquid would be homogeneous. In practice this is not normally possible. Random packings tend to disintegrate, choke, and settle unevenly, and consequently channelling of both liquid and gas is caused, with the inevitable reduction in the efficiency of the tower.

So far as symmetrical packings are concerned, there are certain general features which by capillary action tend to aggregate the liquid into small streams, which cannot then moisten the whole of the lower layers of packing. Such features are :—

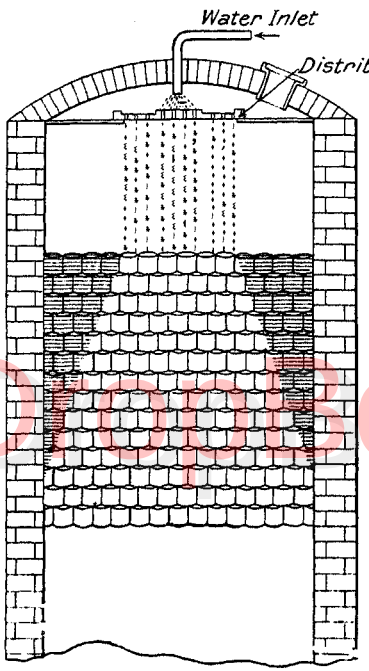

FIG. 70.—Wastage of Tower Space caused by poor Distribution.

1. *Sharp edges or grooves.* The capillary effect on the edge of a glass plate is very well known. Packing materials which have sharp edges in contact therefore should be avoided. This effect occurs for example in the ring and star packing, where the star is made as a loose central fitment for the ring. The vertical lines of contact tend to cause channels of liquid, instead of allowing the latter to spread evenly over the inside of the ring. Such a defect also occurs with the type of packing shown in Fig. 62 (H). Here the liquid tends to aggregate into the hollow channel formed by the shape of the ring, and to flow in a relatively heavy stream down the tower, rather than to spread out evenly over the surface of the filling.

Similarly with the filling shown in Fig. 62 (K). Here the corners act as liquid-collecting channels and prevent adequate distribution. A filling material which has horizontal grooves is also liable to have the defect of causing the liquid to

" channel," especially if the filling (e.g. a grooved tile or plate) is not set accurately level.

Where packing is provided with vertical grooves the capillary effect of the grooves in spreading the liquid will be beneficial provided that the grooves are sufficiently small.

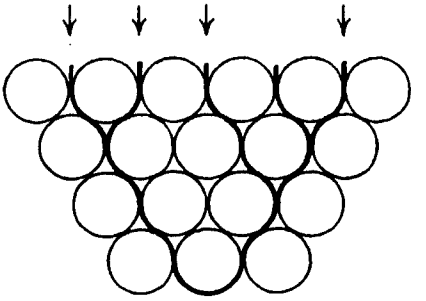

FIG. 71.—Uneven Distribution caused by irregular Ball Packing.

The greatest homogeneity of distribution with symmetrical packings should be obtained with a smooth spherical packing provided that it is carefully packed. Here the capillary effect of adjacent surfaces is such as to cause the liquid to be spread evenly over the mass. If, however, the balls used in the packing differ in size and surface, or are unevenly packed, the filling is a most suitable one for causing liquor channels, and in consequence an incompletely wetted and inefficient tower.

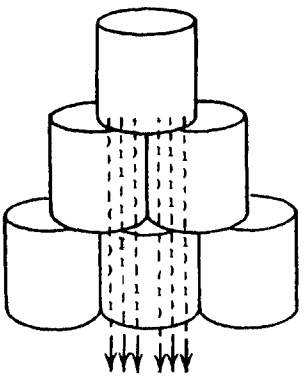

FIG. 72.—By-passing of Packing Layers by Drops of Liquid.

2. *Packings which cause the liquid to fall in drops or streams from one layer to another.* With the circular packing previously mentioned it is practically impossible to have streams or drops of liquid falling from one layer of packing to the next. The liquid consequently attains but little momentum and remains as a thin film which tends to spread over the contact surfaces. With a filling such as stoneware rings, however, it is inevitable that a certain amount of liquid must fall from the lower edge of one row of filling material some distance down the tower before hitting the surface of another element. This has been illustrated in Fig. 72, and it is quite probable in practice that this occurs to an appreciable extent. With

filling materials which have a greater tendency to collect the liquid into drops or streams, the amount of such by-passing which goes on is considerably increased.

It must also be pointed out that if the filling material is of such a shape and surface that it will distribute the liquid by capillarity or surface-tension effect, it is undesirable to collect the liquid into relatively large drops at intervals in the tower, as the liquid must then travel some distance again before the filling is homogeneously wetted in the next lower section (see Fig. 70).

Filling materials, for which it is claimed that they force the liquid to drop from one layer to the next, are not necessarily the more desirable for that reason. The fall of liquid from layer to layer in this manner has two important advantages, however :—

(*a*) The danger of channelling, which is always possible with a filling material spreading the liquid by capillary effects, is avoided, though probably at the expense of some slight loss in efficiency.

(*b*) The impact of the liquid on successive layers of packing causes a small amount of extra distribution.

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A choice has to be made, therefore, between a circular filling, spreading the liquid by capillary effects, and a cylindrical filling, which is apt to short-circuit layers of packing and to cause uneven distribution in this way.

The distributing action of the filling material with respect to the gas is also important, since channelling of the gas is just as likely to occur as with the liquid. With the simple cylinder packing previously described, for example, the tower is divided up into a number of tubes which are more or less separate. The mixing of the gases is apt to be inefficient in consequence, particularly if the gas velocity is high. The ideal filling material in this respect is one in which the line of travel of the gas is continually altered, and is made to impinge as frequently as possible on wetted surfaces, so that the gases are thoroughly mixed as they pass up the tower.

An even circular packing gives good results in this direction, and the Nielsen packing, by giving the gases a whirling motion, is particularly effective in this respect, as is also ring packing provided with a central spiral. The author has found a com-

bination of ring packing and propeller packing very efficient, the towers being packed with alternate layers of 2 feet to 3 feet depth of the different types of packing. This was found to give homogeneous mixing of the gas, while maintaining the conditions of high free space and scrubbing surface.

Drainage of Tower. Certain types of packing retain considerable amounts of the absorbing liquid, e.g. coke and broken brick absorb considerable quantities of liquid. The effective weight of the packing is enormously increased in consequence, the working of the tower is very inelastic, and the effective drainage of the tower is almost impossible. If the tower requires to be cleaned and repacked, it has to be flushed down repeatedly with water, producing large quantities of very dilute and useless acid. It is important, therefore, to use a non-absorbent packing, which is also self-draining. Packings which contain or form liquid traps should be avoided, not only on account of the storage of liquid so retained in the tower and the difficulty of drainage, but also because the tower is not readily susceptible to altered conditions of absorption. Finally liquor pockets offer relatively little absorbing surface, and so are inefficient. This type of packing includes those with hollows on the upper surface and plate packings of the Lunge-Rohrmann type.

Durability and Chemical Action. Most modern stoneware and earthenware is quite resistant to the action of dilute nitric acid. Glass is an ideal material so far as chemical resistance is concerned, but it is fragile and costly and requires skilled labour to pack towers with it. Stoneware is preferable to earthenware for packing material. The stoneware should be homogeneously burned, i.e. the material should not be resistant on the surface only. Glazed materials should hence be regarded with suspicion, as it may mean that once the surface is cracked, disintegration may be caused by the nitric acid, and ultimately cause a subsidence in the packing.

From the point of view of absorption efficiency, the surface of the packing element should be left rough, but preferably non-porous. With most nitric acid absorption systems the effect of temperature on the disintegration of the packing

material does not enter into account, since the entering temperature of the gases should not exceed 40° C.

Filling elements should be of simple construction and substantially made. The more complicated and delicate the construction of the element, the more liable it is to fracture in transit and in packing in the tower, and the less able is it to support the weight of the upper layers of packing. It is usually the case with such elements also that the slightest defect renders them useless.

Despite the theoretical advantages of some of the more complicated types of packing, it is advisable to use an element of quite simple construction. The thickness and weight of the element are matters of practical convenience, but it should be borne in mind that the larger the volume displaced by the material of the element, the less the available free space, and the greater the weight and pressure of the packing. The material should be made only just stout enough, therefore, to bear the weight of superimposed layers of packing, and to be safely handled by unskilled workers. In this connection it is a common device in the smaller absorption towers to provide slate slabs pierced with holes at intermediate points in the tower, to act as supports for the weight of packing in the section of the tower above them. This device enables a thinner and lighter packing to be used, with consequent increase in the available free space in the tower.

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Symmetry and Cost of Filling Material. The cost of a tower packing is made up of two parts:—

(*a*) Prime cost of filling material.

(*b*) Labour cost of packing the tower.

It is evident that the factor of initial cost of the filling material is of great importance, and often outweighs all other considerations. For example, the Norwegian Hydro-electric Company build large towers with very thick walls, because the cheapest filling material to hand is broken quartz and granite, and the quantity of filling material required is so enormous that only the cheapest raw material can be used, irrespective of its efficiency, etc., as compared with other scientifically designed packing materials.

Although there are quite a number of ingenious fillings on the market, therefore, they are little used in absorption

practice owing to their initial cost. Elements of complicated structure which require to pass through several operations before completion cannot hope to compete with an element of simple and cheap construction which may not be quite so efficient.

The labour cost of filling the tower will also vary with the degree of complexity of the element, and whether or not the design is a symmetrical one. The ordinary absorption tower is usually round, and the filling element should be such as can be packed in the tower without having to fill in the edges with broken material. The type of filling that is readily adaptable to either round or square towers is of course the most advantageous.

It is evident also that such types of tower fillings as horizontal plates or tiles, glass strips, cell packings, etc., will require skilled labour to pack them effectively in towers. With the simpler symmetrical fillings, however, the packing can be done by ordinary unskilled labour at very much less cost.

To sum up, therefore, the ideal packing for absorption towers for nitrous gases should fulfil the following conditions:

1. It should give the greatest possible free space, combined with the greatest possible scrubbing surface.
2. It must have a low initial cost.
3. It must be simple and durable in construction and easy to pack into square or round towers.
4. It should not give any appreciable lateral pressure, and should be self-supporting.
5. It should not be such as will accumulate dust or acid.
6. It should cause good distribution of the gas and liquid.

It is considered that, of the modern fillings, the combination of ring and propeller filling previously suggested comes nearest to satisfying the above demands. Up to the present very little accurate comparison has been made of the relative advantages of the better types of filling materials in large-scale operation. Such determinations would be somewhat expensive to carry out. It is certainly the case that so far as Nielsen packing, ring packing, and Guttmann ball packing are concerned, the efficiency is not widely different, if the *capacity* of the system is not taken into account. If in addition, however,

such points as prime cost, labour cost in filling, resistance to gas flow, lateral pressure, etc., are examined in connection with each one, it is clear that sharp differentiation is possible which enables a choice to be made between them. It should also be borne in mind that where the resistance of the filling material and its lateral pressure, etc., may be of little moment in a small stoneware tower, the influence of these factors is magnified considerably as the height and diameter of the tower is increased.

Relative to the use of fine quartz as a packing material, Moscicki[1] puts forward claims for the use of quartz of very small diameter as packing material (0·1–0·2 cm. cubes). He states that this packing has a very high factor of scrubbing surface and the distribution of absorbent is very even. He proposes at the same time, however, to alternate these absorption chambers with unpacked oxidation chambers, and here lies the crux of the whole question.

The type of absorption tower which has up to the present been developed is based on the assumption that the provision of oxidation and absorption space in the same tower is equivalent to the alternate absorption and subsequent reoxidation of the regenerated nitric oxide as two separate stages. In fact, it is not, as will readily be seen by a consideration of the reactions involved. The absorption of N_2O_4 molecules in water gives rise to nitrous acid and nitric acid. The former decomposes into nitric acid and nitric oxide, and the nitric oxide must subsequently be re-oxidized. It makes a great difference, however, whether or not that nitric oxide is re-oxidized in the presence of liquid absorbent. The velocity of oxidation is at first rapid, and then falls off as the concentration of NO decreases. There will be formed almost instantaneously, therefore, molecules which will react effectively towards water as N_2O_4, the result being that nitrous acid is exclusively formed, and must subsequently decompose into nitric acid and nitric oxide. If however the nitric oxide originally present had been allowed to oxidize in the absence of liquid absorbent, it would, given sufficient time, have been oxidized completely to N_2O_4 molecules. This would then have given both nitric and nitrous acids on dissolving in

[1] *Chimie et Ind.*, **2**, Nos. 11–12, Dec., 1919.

water, and an inspection of the equations concerned will show that the amount of nitric oxide regenerated in the one case is twice that in the other. In other words, the system of allowing the regenerated nitric oxide to oxidize completely to nitrogen tetroxide doubles the capacity of the actual absorption tower. On the other hand, the time required for the complete oxidation of nitric oxide to the tetroxide is considerable, especially when the gas is dilute. The total capacity of the system would therefore be decreased if complete oxidation to N_2O_4 molecules were aimed at.

It is quicker to allow the nitric oxide to form only N_2O_3 and a little N_2O_4, and to allow this oxidation to go on in the presence of the liquid absorbent. Although only one-third (approx.) of the resulting nitrous acid is converted into nitric acid, the cycle of reactions is so much quicker as to be advantageous over the alternative system, when the oxides of nitrogen are very dilute. This is the underlying consideration in modern absorption practice. As much oxidation as possible is allowed to go on in the towers, by using packing with high free space, but the oxidation is allowed to take place in the presence of the liquid absorbent.

CHAPTER V

GAS CIRCULATION AND MEASUREMENT

The water-absorption system entails the handling and circulation of considerable volumes of gas in which the amount of oxides of nitrogen is continually decreasing, as the gas is passed through the system. The effective manipulation of such volumes of gases is a problem which demands very careful thought, since the complete recovery of the oxides of nitrogen present can only be effected by a very accurate balancing of the cycle of reactions, and by ensuring that the gas remains sufficiently long in the system for adequate scrubbing to be effected. For this reason the question of gas circulation in its bearing on the efficiency of the plant as a whole needs special consideration. It is evident also that the accurate measurement of gas volumes and gas velocities must form an integral part of the operation of absorption systems, and in this chapter it is proposed to give a brief description of the methods of gas measurement which are applicable to ordinary absorption-plant conditions, and which at the same time give a sufficient degree of accuracy for the purpose in view.

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Gas Circulation. Theoretically, it is advantageous to push, rather than pull, the nitrous gases through an absorption system, for the following reasons :—

1. The linear velocity of the gas is lower, particularly in the towers remote from the fan.

2. The extra pressure on the gas facilitates absorption to a slight extent.

3. The amount of air leakage into the system is very much reduced.

On the other hand, it is very difficult to make an absorption system absolutely gas-tight. Taps from the towers to the elevator systems must be permanently open in continuous working, and if they are luted the gas pressure upsets

the balance of the air lifts. (This would not apply to systems using pump circulation.) A disadvantage of working the system under pressure would hence be the loss of nitrous fumes by leakage, which would entail a considerable loss in efficiency and would be a nuisance in addition. The system is usually operated therefore under a slight suction, which should be the *lowest* suction required to keep the plant just free from outward passage of nitrous gases.

Dampers. In order that the suction (and hence the gas velocity) may be carefully regulated, the pipe system should

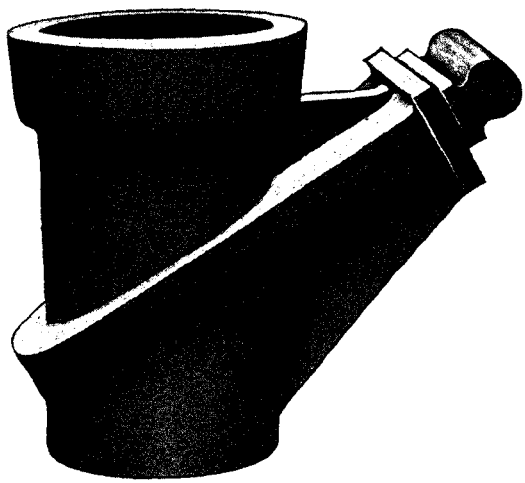

FIG. 73.—Damper for Stoneware Pipes.
Oates & Green, Ltd.

be provided with well-fitting, adjustable dampers. A common type of such is shown in Fig. 73, and with a steady-running fan and even flow of absorbent down the towers, the operation of this damper should be guided almost exclusively by the nitrogen oxide content of the inlet gas to the absorption system. By fitting manometers at suitable intervals along the tower system the draught may be readily controlled and steady, efficient operation rendered more certain.

Draughting System. The suction at the end of the system may be obtained in three ways :—

1. By chimney.

2. By fan.
3. By air or steam injectors.

The type of draughting apparatus used will depend very largely on the amount of gas to be handled, the resistance of the packing material, size of towers, and other special conditions.

Chimney. A chimney is a convenient form of draughting apparatus for small systems, where a very "free" packing material is used. The draught required at the end of a system of eight small towers is only 1–1½ inch water gauge, and most chimneys of 180 feet to 200 feet in height will give this pull, provided that the chimney is not being choked with large volumes of other flue gases, etc. There is very little elasticity in the system, however, and it has a number of other disadvantages. For example, a source of hot gases must also be available, and consequently a wastage of heat is bound to occur. In addition, leakage of acid gases into the chimney may cause serious disintegration of the cement, unless an acid-resisting cement is used in its construction, in which case the initial expense is heavy. Finally, the amount of draught may vary appreciably with the prevailing winds and with the weather. Such a type of draughting was used successfully, however, at one of the English Government factories (1915–18), the chimney, 220 feet high, being built of Nori acid-proof brick and "Doubleset" acid-resisting cement.

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Fans. Where the absorption system is large, and the resistance of the packing very great, a suitable type of fan is essential. There are four types of material available for the construction of these fans—stoneware, regulus, aluminium, and iron-silicon alloys. Of these the first two are by far the most satisfactory at present. The present types of fan in iron-silicon alloys are unsuitable for draughting nitric acid systems. Owing to considerations of strength and speed, they cannot develop much more than 1 inch water-gauge, and owing also to the weight of the propellers, etc., the power required to drive them is out of all proportion to that required for the other available types of fan.

The illustrations of stoneware fans, etc., made by Messrs. Kestners, Limited, will indicate the type of fan most commonly used in this country for draughting absorption and nitric acid

systems. Regulus metal is more commonly in use with sulphuric acid than with nitric acid systems, but both can be used with advantage and efficiency. The stoneware fan is essentially a low-pressure fan, and is operated at 400–1,000 revolutions per minute, with capacities varying from 250–2,500 cubic feet per minute against a water pressure of $\frac{3}{4}$ inch.

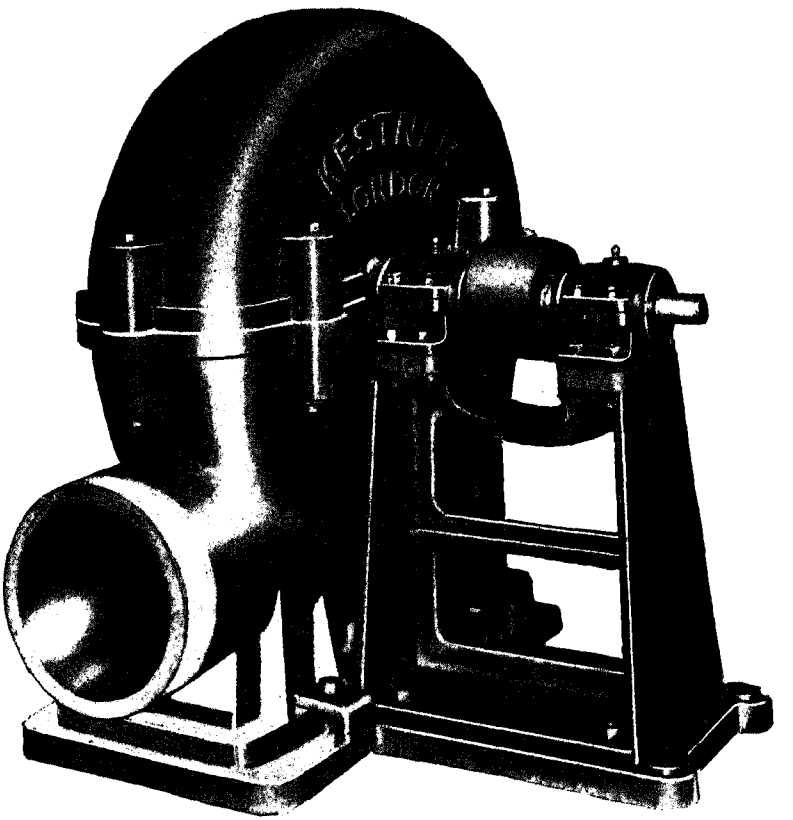

Fig. 74.—Stoneware Fan for Draughting Absorption Systems.

The useful feature of such fans is that the upper part of the case can easily be removed for examination of the impeller, which is secured to a protected steel shaft.

The use of aluminium fans in absorption systems has developed considerably in recent years. Aluminium is resistant to concentrated nitric acid, the rate of attack being greatest

with dilute acids, especially if hot. At ordinary temperatures, however, aluminium fans have a reasonable life in contact with nitrous gases. Such fans are often placed between successive towers in the case of very large absorption systems, since the

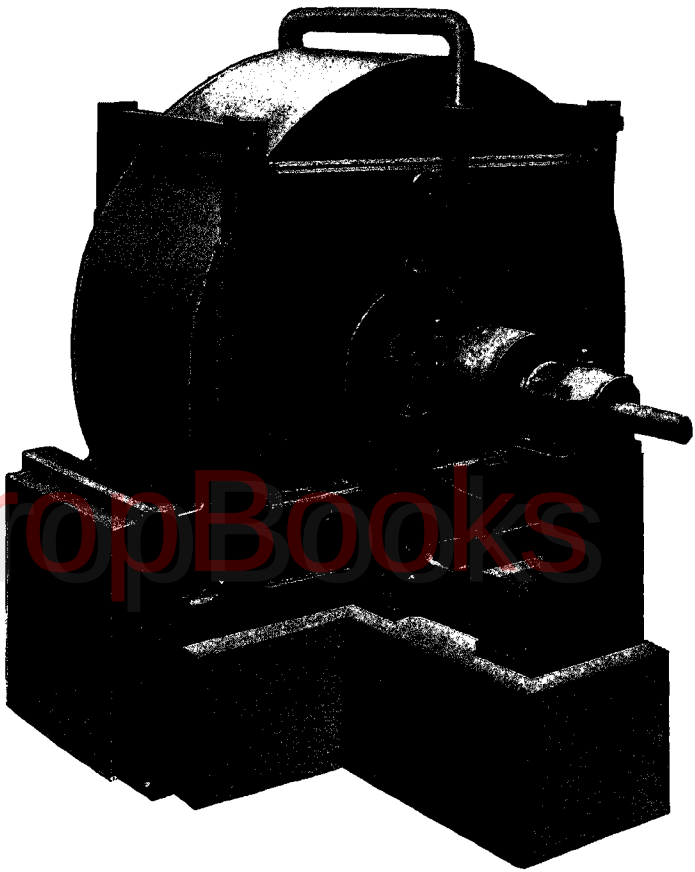

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FIG. 75.—Regulus Metal Fan (Low-pressure).
Kestner, London.

pressure drop in the gas from tower to tower is very high. This was the arrangement adopted at the Muscle Shoals Nitrate Plant at Alabama, U.S.A., although no experience of value as to the life of the fans was gained before the plant closed down. A similar device is in operation at the plant of

the Norwegian Hydro-electric Co. at Rjuken, and with the gases being dealt with there, aluminium fans appear to give very good service. High-pressure fans are seldom necessary for ordinary types of absorption systems. They may be obtained, however, to give a suction up to 10 inch water gauge, with capacities up to 6,000 cubic feet per minute, the speed varying from 1,200–2,000 revolutions per minute. The centri-

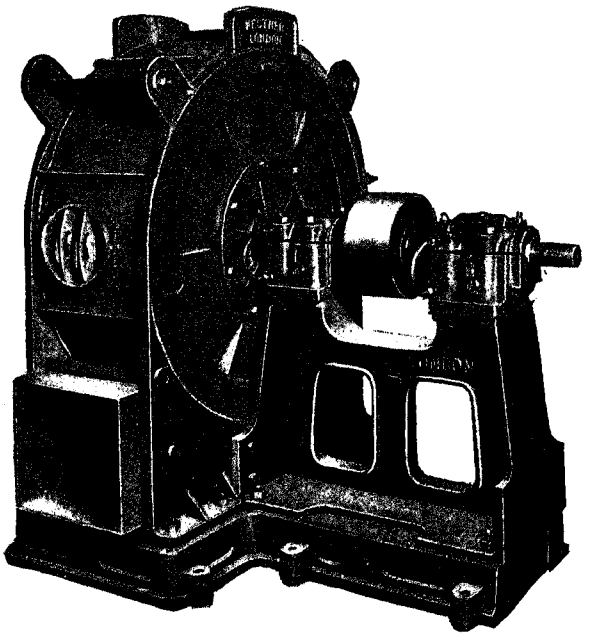

FIG. 76.—Regulus Metal Fan (High-pressure).

fugal action of the fan in an absorption system is such that a very appreciable quantity of acid mist is condensed inside the fan casing, which should be provided with a suitable drain cock, connected to an outside sump from which the weak acid may be collected, or alternatively the fan is mounted on a concrete base at such a height that the acid deposited may be run directly into carboys or other suitable storage vessels. The discharge of such fans should of course be vertical and on the upper side of the fan.

Injector System. The use of stoneware fans is attended

with certain disadvantages such as those of weight and fragility, while in the case of regulus metal fans it is desirable that the gases should not come directly into contact with the impeller or fan casing. A type of draughting system designed to overcome this difficulty is shown in Fig. 77. The principle is that of an injector. A high-speed fan drives a jet of air through an orifice expanding into a pipe of much larger diameter, with the result that a draught is induced which is quite sufficient for most small types of absorption systems. This type of draughting system is useful inasmuch as the fan used need not be acid-resisting and consequently the practical difficulties of construction largely disappear. The arrangement is very inefficient, however, compared with a direct-acting fan, and the power cost is naturally much heavier.

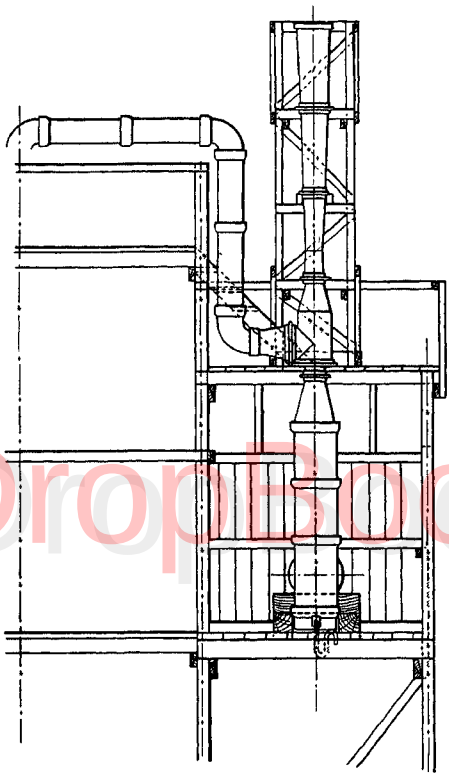

FIG. 77.—Diagram showing Method of producing Induced Draught.
From *Technical Records of Explosives Supply*, 1915-18, No. 1.

The use of steam injectors for draughting is quite similar in principle to the air-injection system just mentioned. There again the injector can be fitted so that contact between the jet and acid gases can be avoided. This is usually done by fitting the jet horizontally (Fig. 78); otherwise it is necessary to use jets of glass, silica, stoneware, etc., in which case the jet is fixed in a different way to the above. The steam jet is

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again a very uneconomical form of draughting apparatus, and the steam consumption even of small jets is excessive. They are very little used at the present time in absorption plants. There is another objection to their use which should be mentioned. In cases where a loss of nitrogen oxides is taking place through the exit, the use of a steam jet causes the production of a fine mist of nitric acid in the neighbourhood of the plant, which has an exceedingly corrosive action on ironwork, besides being otherwise objectionable.

The size of fan to be used in a system is fixed by the volume of gas to be dealt with and the resistance of the packing. A set of eight small absorption towers 3 feet × 14 feet will usually deliver 25–30 tons of nitric acid (as 100 per cent.) per week of continuous running. Taking the figure of 25 tons and assuming

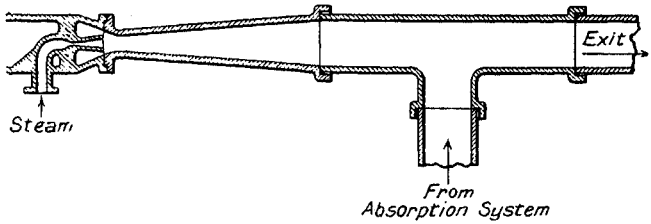

FIG. 78.—Stoneware Injector, showing Steam Connection.

the inlet gas contains 10 per cent. by volume of nitrogen tetroxide (as NO_2), the fan would be required to draw approximately 400 cubic fect of gas per minute, not allowing for air leakage. This amount of gas could be amply dealt with by a low-pressure fan with 12 inch diameter suction running at 750 revolutions per minute.

It must be emphasized here again that the practice of fitting high-capacity fans to an absorption system, because the rate of gas flow through the towers is apparently insufficient, is strongly to be condemned unless it is first ascertained whether or not the resistance of the packing material is the cause of the trouble. The possibility of a subsidence of the packing material should be allowed for, even when symmetrical, scientific packings are used. Where it is found that the volume of gas to be dealt with requires a fan of considerably greater output than theoretically necessary, it will usually be found

that the repacking of the towers will be the cheapest remedy in the long run.

Acid Mist. It is a matter of common observation that the exit gases from an absorption system contain appreciable quantities of nitric acid vapour. This mist is formed to some extent even when alkaline absorbents are used in the end towers of the system, and is somewhat similar to sulphur trioxide in the difficulty of its condensation. Taylor Capps and Coolidge [1] used a form of Cottrell precipitator to remove the mist, similar to that used in sulphuric acid manufacture, and obtained nitric acid containing 15–25 per cent. HNO_3. The formation of this acid mist takes place quite readily when the gases contain more than a certain percentage of moisture. In large-scale work the percentage of nitric acid in such acid mist has been found to be as high as 40 per cent. HNO_3, and the loss due to acid carried over in this way may be considerable.

In many systems where the gases are drawn directly through a fan at the end of the system, a small amount of such mist is centrifuged out, and the quantity of "fan drip" acid so obtained gives some idea of the total loss which may occur in this way. In present-day absorption practice, even when using a final alkaline absorbent, the efficiency obtained does not exceed 97–97·5 per cent. as a maximum, calculated on the basis of total fixed nitrogen recovered. The 2·5–3·0 per cent. loss obtained includes a handling loss of approximately 1 per cent., the remainder being due to the escape of acid mist and nitric oxide from the system. Where no final alkaline absorbent is used, the efficiency of the absorption system lies between 92–95 per cent. if fairly concentrated nitrous gases are available. In this case the loss due to acid mist lies between 2·5–3 per cent. of the total output of the towers.

The Badische Anilin und Soda Fabrik [2] propose to dissipate a nitric acid mist by means of a high-tension electric discharge. Their apparatus seems to be quite similar to the Cottrell and Lodge precipitators used in this country. A recent French patent [3] gives details of an electrical precipitation apparatus which has been used in the nitric acid industry. The potential difference used varies from 20,000–40,000 volts. The elec-

[1] *J. Ind. Eng. Chem.*, 1918, **10**, 270.
[2] D.R.P. 233,729, 1910. [3] Fr. Pat. 463,821, 463,825, 463,830.

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trodes consist of aluminium plates, one of which is smooth and the other covered with asbestos fibre. It was found that with an apparatus of this type nitric acid up to 1·41 sp. gr. (65 per cent. HNO_3) could readily be condensed.

It seems very probable that the application of electrical precipitation on a much wider scale to absorption practice is a very likely development in the near future.

Measurement of Gases. The measurement of the amount of gas passing through an absorption system is essential to scientific control and can be carried out in a number of ways. With small systems draughted by a single fan, the amount of gas being drawn through may readily be calculated from the speed and diameter of the fan, provided that the delivery of the fan under standard conditions is known. Similarly where standard boosters and blowers are used for handling the gas, the rate of discharge under standard conditions is usually known. Where such is not the case, however, and where also measurement of air or other gases entering into the process is essential, a number of methods may be adopted.

A simple method of determining the amount of an inlet or exit gas containing nitrogen oxides is to determine the linear velocity of the gas in the main of known diameter. Two holes are made in a length of main, free from bends and elbows. These holes should not be less than 30 feet apart, and preferably 100–150 feet. Some concentrated ammonia is injected at a given instant by the observer, and the time taken for the white cloud of ammonium nitrate to appear at the second aperture indicates the centre or greatest velocity of the gas. The method is quite simple to carry out, and very useful for obtaining an approximate idea of the volume of gas passing.

There are a number of meters on the market, however, which can be used where more accurate measurement of gases is necessary. These depend mainly on differential-pressure measurement, but others measure the volume of gas directly. The general types are as follows :—

1. Those based on the Pitot tube.
2. Those based on the Venturi principle.
3. Turbo-meters.
4. Electrical meters.
5. Wet and dry volume meters.

Pitot Tube. The Pitot tube consists essentially of two constituent tubes, one with its opening at right-angles to the direction of gas flow, the other curved so that its opening is towards the gas flow and parallel with it (Fig. 80).

The tube A is preferably made in the form of a jet in order to minimize convection effects. Its aperture may also be turned parallel with the gas flow (Fig. 79), but the differential pressure set up under the two conditions is not, of course, identical. The static pressure is measured by the tube A, while the tube B measures both the static pressure and also the pressure due to the velocity of the gas. The resultant pressure, which is the difference between the pressures

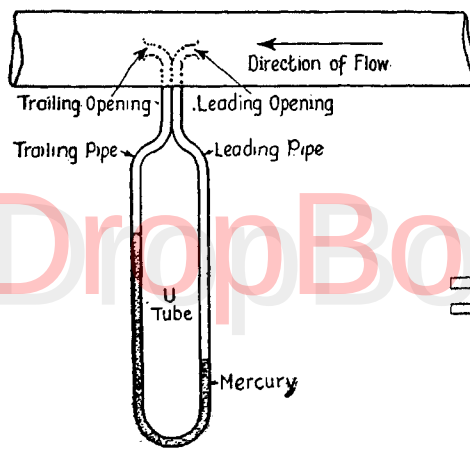

FIG. 79.—Elementary Form of Pitot Tube and Meter.
British Thomson-Houston Co., Ltd.

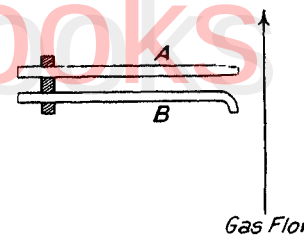

FIG. 80.—Pitot Tube.

measured by A and B, is proportional to the square of the velocity of the gas. As an approximation it may be taken that

$$\text{Differential pressure in inches of water} = \frac{\text{Wt. of gas in lb. per cub. ft.} \times \text{Square of velocity of gas in ft./sec.}}{155}$$

A convenient and portable form of Pitot-tube meter is Fletcher's anemometer (Fig. 81).

This consists essentially of the Pitot tubes of glass (a, b), each of which is connected to one arm of a manometer (c, d). The measuring liquid used in the manometer is a mixture of

ether and chloroform of sp. gr. = 1. This mixture is preferable to water in that it possesses greater mobility and does not wet the sides of the tube.

When in use the base of the instrument is first levelled and the inclination of the manometer tube adjusted to an angle with the horizontal depending on the velocity of the gas to be measured. If the gas velocity is high (about 40 feet per second) the position at 30° is used. For lower velocities the other inclination (one in 10) is used.

The tubes from the Pitot tube are connected through a "reverser" (*e*) to the manometer. The height of the liquid in either arm of the U tube is measured, and then by turning

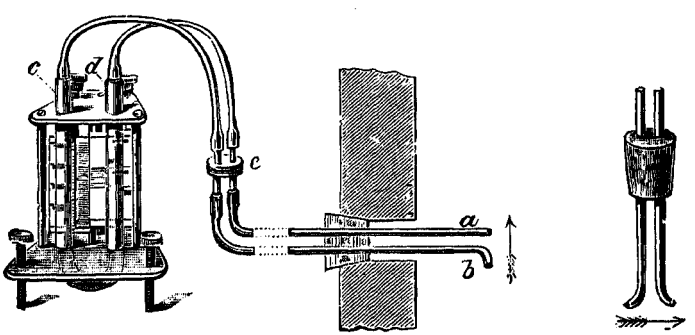

FIG. 81.—Fletcher's Anemometer.
Baird & Tatlock, Ltd.

the reverser the reading of the U tube is reversed, and the level is read again in the *same* arm of the U tube. The difference in the two readings gives twice the actual pressure head. The gas velocity v is then calculated from the expression $v = 46{\cdot}67\sqrt{h}$, where h = height in inches supported in the manometer tube by a liquid of sp. gr. = 1. A correction for temperature is applied by dividing the value so obtained by a value K where $K = \sqrt{\frac{273 + T^\circ}{273 + t^\circ}}$ where $T = 15^\circ$ C., t = observed temperature.

The advantage of this apparatus lies in its portability and ease of manipulation, as it may readily be carried from one part of the plant to another, and gas-velocity measurements made quite rapidly. It is the apparatus most commonly used

at present for intermittent measurements of gas velocities where a high order of accuracy is not required.

The Pitot tube has been adapted for the construction of meters for permanent installation in a pipe-line, giving a constant record of gas velocity, which may be transmitted, if required, to a recording chart. Fig. 82 shows the fitting made by Messrs. Geo. Kent, Ltd., Luton, for this purpose. The figure shows the Pitot-tube fitting screwed into the gas main. The upstream and downstream pipes are connected to

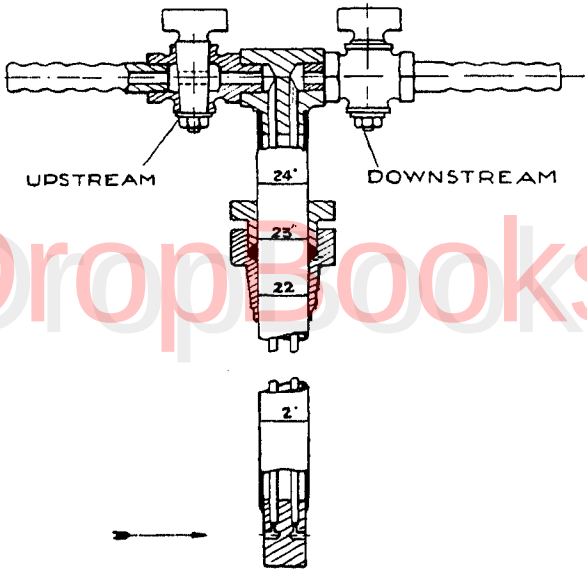

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FIG. 82.—Kent's Pitot Tube.

George Kent, Ltd.

a suitable manometer for measuring the differential pressure set up.

The British Thomson-Houston Co., Rugby, have adapted the principle in rather a different and very compact fitting, known as the velocity nozzle plug (Fig. 83). The tube projecting into the main is divided into two compartments, each being a half-segment of a circle, with a number of holes pierced in the circumference. One set of holes faces the direction of gas flow, the other faces in the opposite direction. A reservoir

is placed on each pressure tube, in order to eliminate oscillations of the manometer liquid.

The Pitot tube is only satisfactory for measuring gases moving with relatively high velocity, which have no suspended impurities liable to silt up the tubes. Fletcher's anemometer is perhaps the least sensitive type of Pitot-tube instrument, but is the most commonly used on account of the ease of manipulation. Generally speaking, a linear gas velocity of 7–10 feet per second represents the minimum which may be measured with reasonable accuracy with this type of anemometer. By the use of more sensitive recording instruments, such as the curved-tube manometer shown on page 224, a slightly lower minimum velocity may be measured, but in such cases it is preferable to use either a venturi-meter or an orifice plate.

The Pitot tube suffers from an additional disadvantage in the case of very wide mains, that the gas velocity is measured only at one particular point (which should be at a distance of one-third the diameter of the main, from the side of the main). In case of turbulent flows the readings may therefore be quite inaccurate.

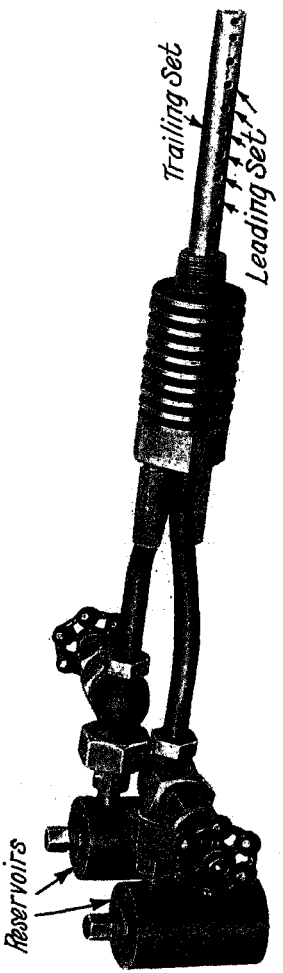

FIG. 83.—Pitot Tube for use with Flow Meters.
British Thomson-Houston Co., Ltd.

The Venturi-meter. Another very useful type of differential-pressure meter is the venturi-meter, the principle of

which has been adapted to the construction of some of the best types of standard meters for gas measurement. A diagrammatic representation of the meter is shown in Fig. 84. The principle of the meter will be evident from a consideration of the diagram. A gas travelling in the direction A, under a pressure P, on meeting the constriction B will set up a differential pressure between A and C in which the pressure on the side A will be the static pressure of the gas P, plus an additional pressure X, proportional to the square of the velocity of the gas and to its temperature, and also to the size of the con-

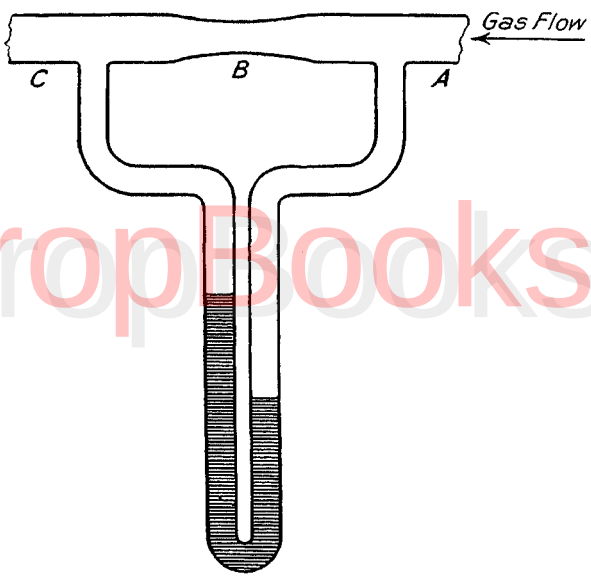

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FIG. 84.—Simple Venturi-meter.

striction B. The pressure at C will be the static pressure P. The differential pressure X is then measured in a manometer, whose leading tubes are taken off at suitable points on either side of the constriction B. By calibrating the manometer for a number of gas flows, the venturi-meter can be made of any desired range. The error usually obtained with such meters can be made less than 1 per cent. The author has used such meters in ammonia-oxidation work for some time, and has found them to give accurate and reliable data provided that temperature variation is excluded, with the added advantages

of simplicity of construction and ease of observation. By suitable care in the construction of the constricted tube (i.e. smooth curves, etc.) all oscillation of the manometer liquid can be avoided, and the provision of pressure reservoirs will also assist this object. The venturi-meter principle has been

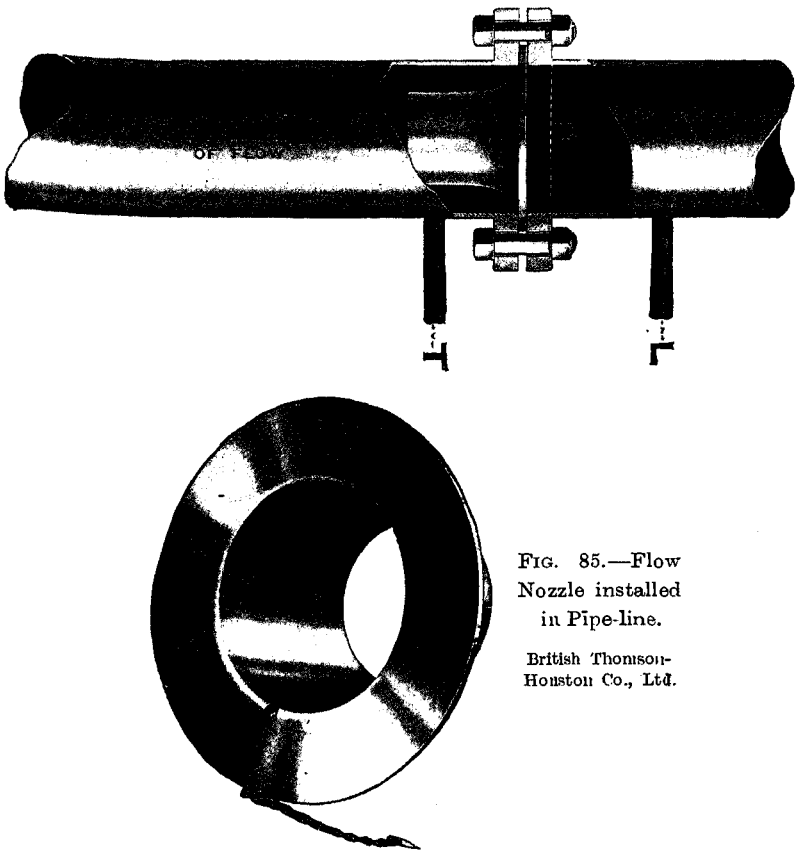


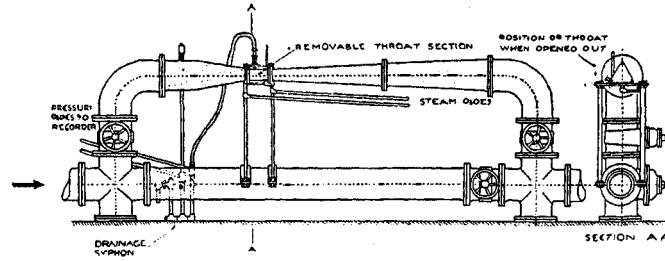
FIG. 85.—Flow Nozzle installed in Pipe-line.

British Thomson-Houston Co., Ltd.

adapted to the construction of accurate practical meters with considerable success in this country, notably by the British Thomson-Houston Co., Rugby, and by Messrs. Geo. Kent., Ltd., Luton.

The meter manufactured by the British Thomson-Houston Co. is shown in Fig. 85. Here the differential pressure is set up by decreasing the effective diameter of the main by

means of a flow nozzle inserted between suitable flanges on the pipe-line. The manometer tubes are taken from the main pipe



"U" (Upstream Cock).

Removable Throat Section.

"T" (Throat Cock).

"H" (Steam Supply Pipe for heating Throat Section during winter months).

"S" (Syphons at foot of Pressure Pipes).

"C" (Curved-tube Manometer for indicating the Flow of Gas).

"B" (By-pass Valve).

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FIG. 86.—Venturi-meter installed in Pipe-line.
George Kent, Ltd.

(L) and from the centre of the flow nozzle (T). The greater the loss of pressure head which can be allowed, the greater the

accuracy obtainable with the meter. In this connection it should be noted that it is preferable to lead one of the pressure arms of the manometer from the centre of the constriction, as the highest differential pressure is thereby obtained, and,

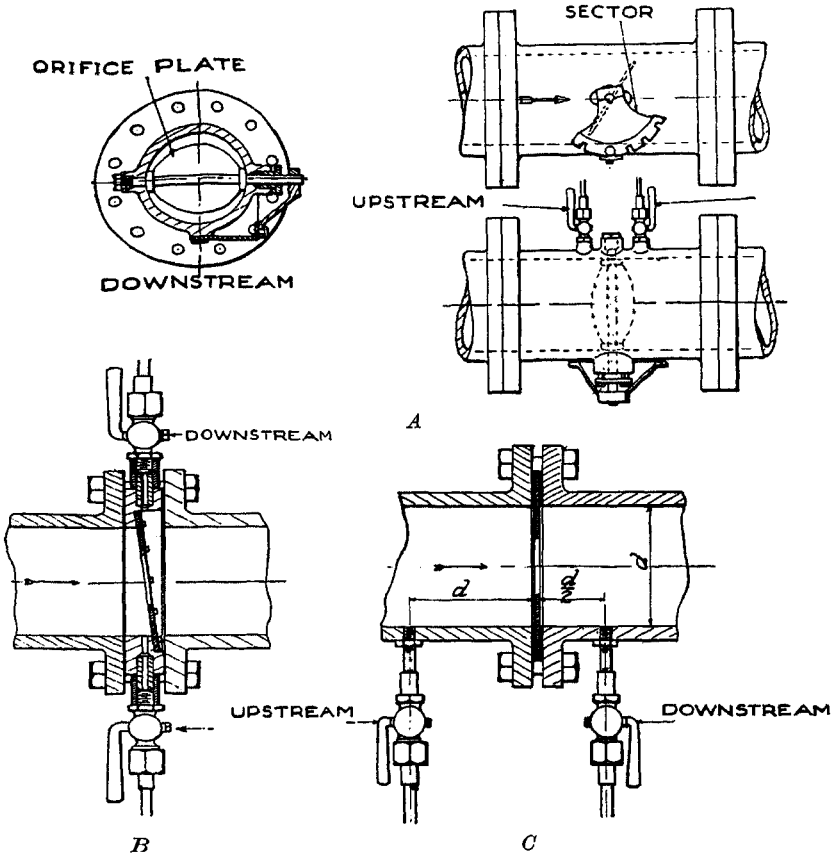

FIG. 87.—Types of Orifice Plates for producing Differential Pressures.
A, "Y" Type; *B*, "S" Type; *C*, "P" Type.
George Kent, Ltd.

further, the oscillation of the gas flow is the least at this point. This is illustrated both in Fig. 85 and also Fig. 86.

The use of a flow nozzle or similar device is not always necessary for the construction of large-scale venturi-meters. The coned pipe may be made part of the pipe-line itself, as in

the meter shown in Fig. 86. The use of such tapered pipes for the construction of venturi-meters, however, is usually limited to mains of 1 inch to 6 inches diameter. The British Thomson-Houston Co., for example, fit them to mains up to 2 inches diameter.

In cases where the mains are of large diameter (2 feet or more), or where it is undesirable to fit lengths of coned piping, the venturi tube may be modified in several ways, but all operating on the same principle, viz. the creation of a differential pressure.

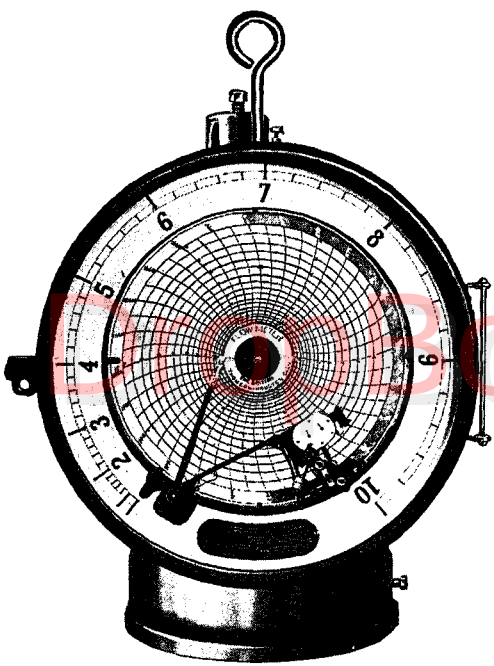

FIG. 88.—Indicating, Recording, and Integrating Flow Meter.
British Thomson-Houston Co., Ltd.

The diagrams in Fig. 87 show various types of "orifice plates" which may be fitted into ordinary flanged pipes to set up the necessary drop in pressure head. These consist essentially of a metal disc with a circular hole in its centre, which disc is inserted into the pipe-line. A certain loss of pressure of the gas in the main is caused thereby, which is measured on a suitable manometer through tubes placed on either side of the orifice plate. Such differential pressure instruments can be adapted to give very accurate measurement of gas flows for industrial purposes, particularly when combined with sensitive recorders.

and integrating recorder made by the British Co. is shown in Fig. 88. This is very where the total quantity of gas which has

passed through the system is required, in addition to the current velocity. Such a recorder is of particular service in large-scale absorption plants, where such data are quite important for the efficient operation of the process and for the rapid determination of the efficiency of the absorption cycle.

Fig. 89 shows a manometer which has been developed in order to provide a more accurate and easily read flow indicator than the ordinary manometer. The difficulty with the latter lies in the fact that since the pressure difference varies as the square of the velocity of gas flow, the scale is exceedingly congested at low rates of flow. This has been ingeniously overcome by curving the tube so as to obtain an equally spaced scale from about $\frac{1}{10}$th the maximum flow upwards. Accurate readings down to $\frac{1}{16}$th the maximum flow can be obtained when using these recorders, and if used in connection with the Y-type orifice shown in Fig. 87, it is possible to obtain readings accurate down to $\frac{1}{100}$th of the maximum flow. The advantage of the venturi-meter lies in the fact that there are no moving parts to get out of adjustment, and, owing to the smooth contour of the constriction, no eddies are set up in the pipe, and consequently oscillation of the manometer liquid is avoided. The meter is immediately sensitive to changes in velocity, and it can readily be used as a direct-reading intrument. Perhaps the most serious disadvantage attached to the meter is that it cannot be used with safety for gases containing suspended matter, dust, tar, etc., owing to the deposition of the suspended material in the constriction, thus causing high readings. This is overcome to some extent in practice by making the throat easily accessible for cleaning.

Venturi-tubes may be installed either horizontally or vertically. The latter method is preferable in practice if the gases are liable to deposit dust, as cleaning is thereby facilitated, and the tubes take a much longer time to silt up.

Turbo-Gas Meters. The rotation of a number of small impellers, by a jet of gas passing along a pipe, has been frequently used as a means of measuring gas flows. The earlier types of instrument consisted of four rotors mounted on a spindle connected with some form of counting mechanism. The great difficulty with the earlier instruments (and one which led to their abandonment) lay in securing frictionless bearings.

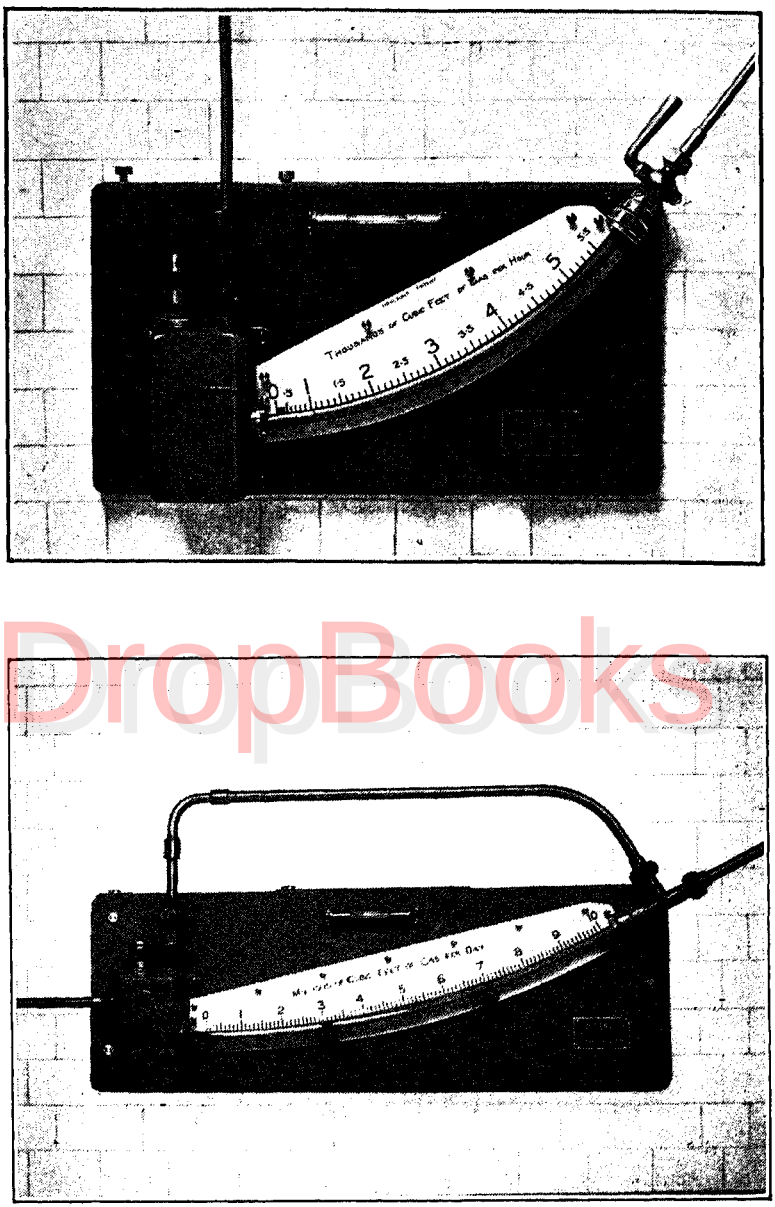

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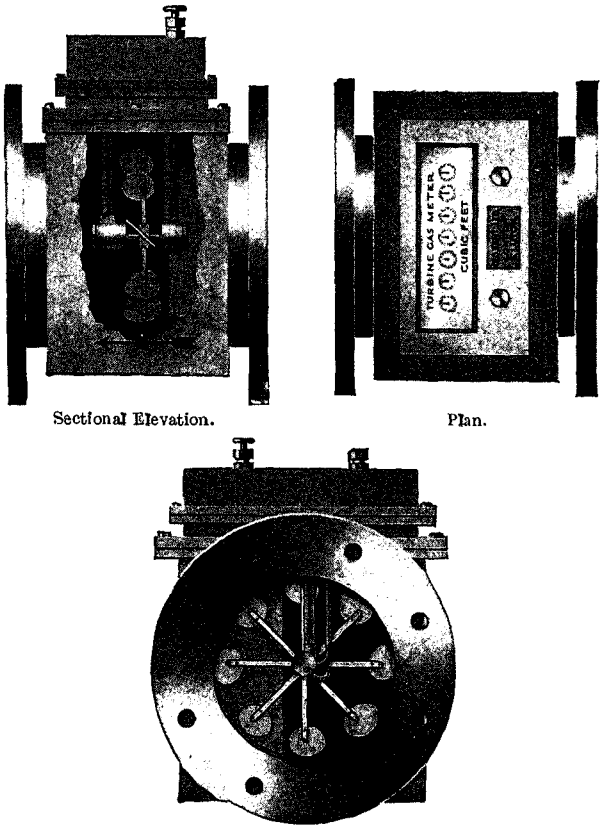
FIG. 89.—Curved-tube Manometers.

George Kent, Ltd.

Furthermore, the presence of dust, corrosive gases, moisture, high temperatures, pressure variations, etc., all contributed to render the meter inaccurate. At the present time, the turbometer has found very little application in chemical industry, owing largely to the corrosive nature of the gases dealt with,



Sectional Elevation. Plan.

End Elevation.

FIG. 90.—The Turbine Gas Meter.
George Kent, Ltd.

and it is normally preferable to use a venturi-tube or other differential-pressure instrument. A useful type of turbine meter, however, is shown in Fig. 90, in which many of the common defects of such indicators have been eliminated.

In this instrument frictionless wheel bearings are used, and

only one jet, instead of several, for discharging the gas on to the rotor. The actual volume of the gas passing is registered by the counter. To convert this to "free" gas, corrections must be made for the temperature and pressure, which amount to about 1 per cent. for 5° F. in temperature, or 5 inches water gauge in pressure.

Electrical Meters. A description of the "hot-wire" meter would be out of place in this volume, especially as its application to the industry under consideration is only in the experimental stage.

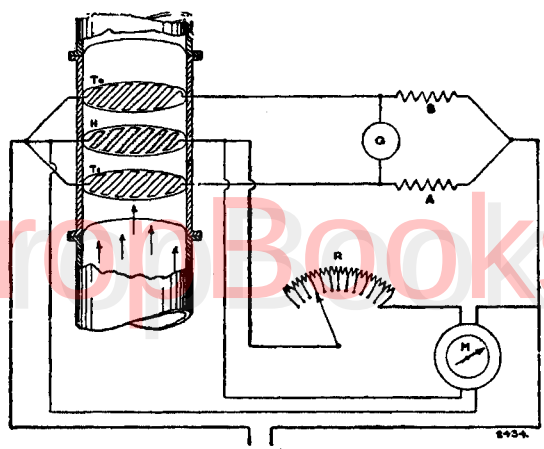


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FIG. 91.—Thomas Meter, showing Electrical Connections.
Cambridge & Paul Instrument Co., Ltd.

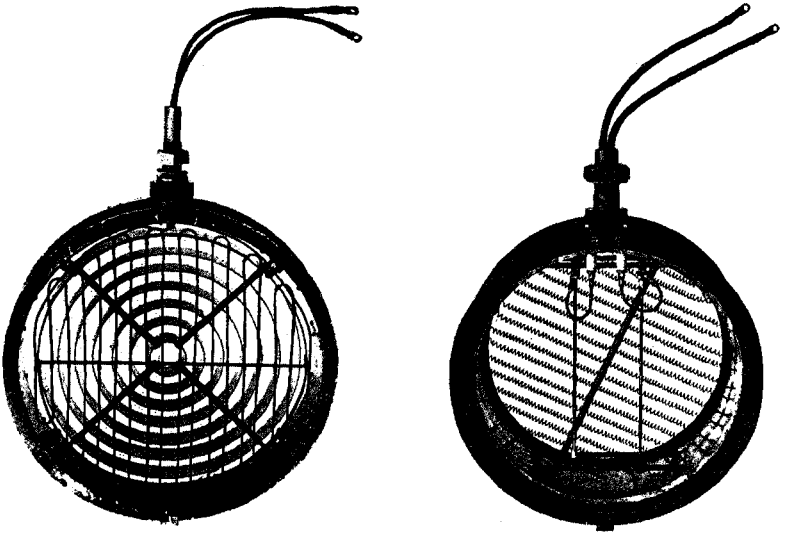
A new and important type of meter which might be briefly considered, however, is the Thomas meter. The principle of operation of the meter consists in warming the gas 2° F., and measuring the amount of electrical energy required to do this. This assumes of course that the quantity of energy required to warm a standard unit of industrial gas through 2° F. is essentially the same, regardless of variation in composition, plant-operating conditions, etc., and this has been found to be true in practice. The essential parts of the apparatus are (Fig. 91):—

(*a*) A resistance heater H which heats up the gas through exactly 2° F. as it flows through the meter.

(*b*) Resistance thermometers T_1 and T_2 fixed on the entrance and exit sides of the heater, which enable the exact temperature rise to be adjusted.

(*c*) A regulator R, which varies the heating current according to the rate of gas flow, so that only sufficient current is used to heat the gas through 2° F.

(*d*) A galvanometer G connected in a Wheatstone Bridge circuit (A, B) with the two resistance thermometers, so that



A *B*

FIG. 92.—Collecting (*A*) and Heating (*B*) Elements in Thomas Meter.
Cambridge & Paul Instrument Co., Ltd.

any variation in their relative resistances deflects the needle to the right or to the left, and is accompanied by variation in the heating current supply.

(*e*) A meter (M) which measures the amount of heating current passing into the heater, and transmits this into terms of cubic feet of gas passing.

The heaters consist of spiral coils of resistance wire wound to and fro inside an insulating drum. The two terminals are brought out at the side and connections are led from them to there gulator and circuit (Fig. 92 (B). The resistance thermo-

meters (Fig. 92 (A) consist usually of a nickel resistance wire, encased in a flexible tube, wound over a circular frame. The tube is lead-covered and sealed so that the nickel wire is protected from corrosion by the gas.

The electrical energy measured is proportional to the quantity of the gas, and independent of its temperature and pressure. The meter has not yet been applied, so far as the author is aware, to the measurement of gases in nitrogen-fixation plants, but certainly offers a new and interesting type of meter giving accurate results with large gas flows, which should find extensive application for gas measurement of all kinds.

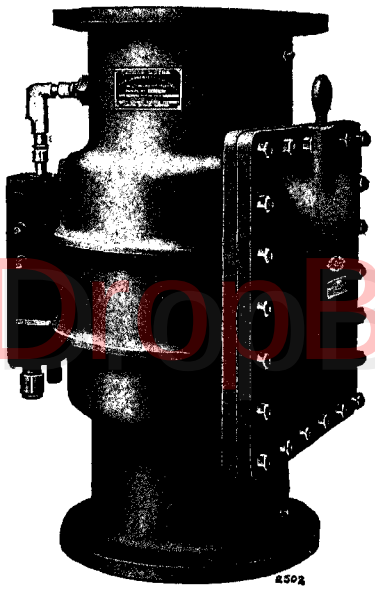


FIG. 93.—Housing of the Thomas Meter.

Cambridge & Paul Instrument Co., Ltd.

Wet and Dry Meters. The principle of the wet and the dry gas meter is too well known to need description here. Their use in the nitrogen industry is very limited, chiefly owing to difficulties of suitable construction material, confining liquid, etc., and, above all, to the fact that where large volumes of gas have to be measured, their size is excessive and their capital cost relatively high. The author has used oil-filled meters as wet meters for ammonia measurement, but the results were quite unsatisfactory. The accuracy was very poor, and the corrosion of the casing very rapid.

The accurate measurement of the acid gases which have to be handled in absorption systems is not carried out in practice as much as is desirable. It is a comparatively simple matter to obtain an approximate idea of the quantities of gas passing through a given system, e.g. by calculation of yields from the

starting products, but this is quite a different matter from the ascertaining of reliable data concerning the balance of a plant cycle, or the distribution of gas to different absorption systems, etc. There is little doubt that in such cases the differential-pressure meter can be adopted, and gives a maximum error of 1 per cent. under ordinary conditions. The forms of differential-pressure meters previously described are, of course, standard commercial products, but it is quite a simple matter in most works for the engineering department to fit up mains on the venturi principle with simple pressure-recording apparatus, provided that suitable means for calibration are available.

It is not necessary to use air for the calibration of venturimeters. In fact, it is often more convenient to use water (or steam) for this purpose, as it can be measured much more easily in bulk than a gas. It is only necessary then to determine the relationship existing between gas and water flows through a given type of orifice.

CHAPTER VI

THE HANDLING OF NITRIC ACID IN THE ABSORPTION SYSTEM

The efficient circulation of the absorbing liquid, and the general transport of dilute and concentrated nitric acids, are operations which probably occupy a larger amount of attention from the chemical engineer than that given to all the rest of the absorption plant. The type of apparatus used for this purpose is at present in a state of flux, since it is unfortunately the case that reliability and efficiency do not go hand in hand in the case of plant for circulating weak nitric acid. The question is further complicated by the range of operating pressures required by the various systems, due to the size of individual tower units, and it is very difficult to lay down hard-and-fast rules for the question of circulation in general. In this chapter it will be endeavoured to discuss briefly the types of apparatus available and their particular merits, but it must be borne in mind, as a principle of operation, that reliability far outweighs considerations of efficiency in the case of absorption plants for nitrous gases, as must necessarily be the case.

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Elevation and Circulation of Nitric Acid

The handling of dilute nitric acid in bulk has been one of the great difficulties to be encountered in all plants for the absorption of nitrous gases. The materials available for the construction of pumps and pipe-lines are very limited, and those at present used for large-scale work are mainly stone-ware, iron-silicon alloys, and aluminium. Of these, aluminium is used only to a limited extent for pipe-lines carrying cold acid, e.g. air elevators. It is also used to some extent for the construction of tanks and vessels to hold concentrated nitric

acid, but it is unsuitable as a material for acid pumps. Most of the present-day apparatus for the transport of dilute nitric acid, therefore, is constructed in either stoneware or one of the several iron-silicon alloys on the market.

The main types of elevating and circulating apparatus used for nitric acid are as follows:—

1. Pumps, which may be further subdivided into
   (*a*) Plunger pumps.
   (*b*) Centrifugal pumps.
   (*c*) Diaphragm pumps.
2. Compressed-air apparatus, which includes
   (*a*) Simple blowing eggs.
   (*b*) Automatic elevators.
   (*c*) Pohle lifts or emulseurs.

Pumps

Plunger Pumps. The use of plunger pumps for nitric acid work has not developed to any appreciable extent, owing to the difficulty in the past of securing rubbing surfaces which would remain liquid-tight over any period of time in contact with nitric acid. Until the development of iron-silicon alloys in recent years, stoneware was the only material available for the construction of this type of pump. The limitations of stoneware for the construction of moving parts are very great. Its liability to fracture, its fragility, the necessity for very thick casings to resist high pressures, are a few examples of its many disadvantages. Practically all such stoneware pumps have a low efficiency and are speedily put out of action by gritty liquids. Once this has happened, a satisfactory repair is almost impossible, and the continual leakage then obtained constitutes a further undesirable feature. One of the few stoneware plunger pumps of reasonable design at present on the market is made by Messrs. Doulton & Co., London (Fig. 94). Generally speaking, the centrifugal pump is more satisfactory than a plunger pump if the construction material is stoneware.

If, however, a suitable construction material were available, it would be possible to construct plunger pumps of relatively high efficiency and possessing the added virtue of reliability. While the ideal material is not yet available, the development

of iron-silicon alloys for this purpose has been attended with considerable success, and has led to the introduction of a new type of plunger pump by Messrs. Kestner, Ltd. (Fig. 95). In this pump a small clearance is given between the plunger and the gland, the gland itself being solid, and consequently no

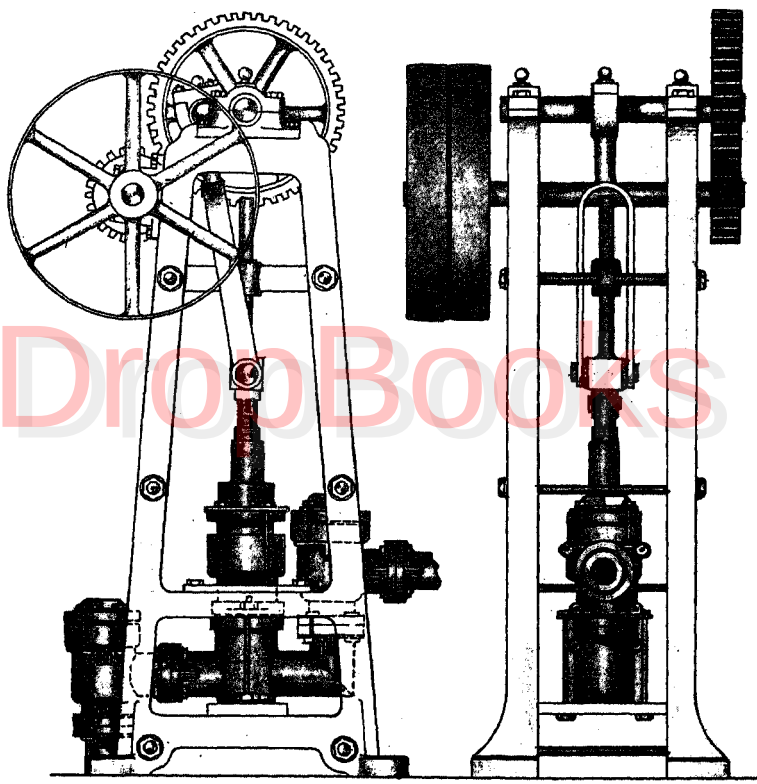

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FIG. 94.—Stoneware Force Pump.
Doulton & Co.

packing is required. The clearance allows a small but definite quantity of the liquid being pumped to leak into an annular chamber placed above the gland, from which it is drained back to the feed tank. As the leakage is extremely small, being about 12 drops per minute, the effect on the pump efficiency

is inappreciable. The pump body, plunger and valves are constructed in ironac. Efficiencies of about 70 per cent. have been obtained with this pump, and it is stated on good authority that small pumps of this type, when lifting sulphuric acid of sp. gr. = 1·72 to a height of 60 feet, give an average efficiency of 69 per cent.

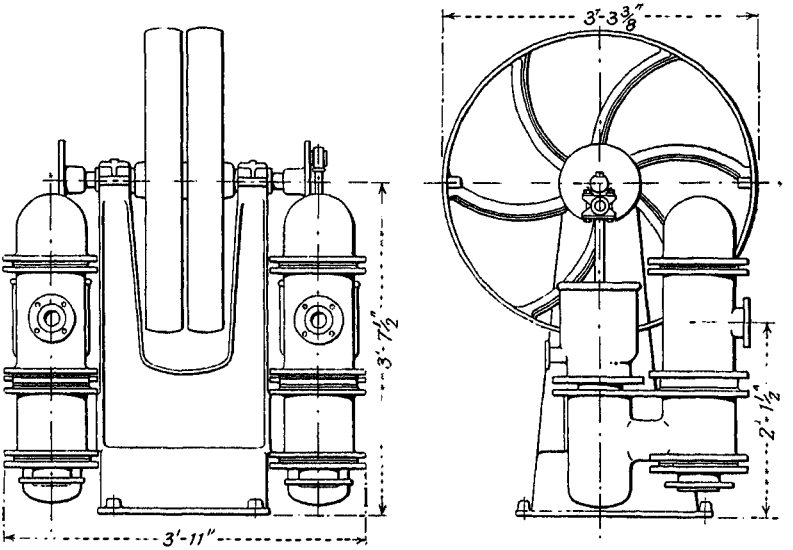


FIG. 95.—Glandless Ironac Plunger Pump.
Kestner, Ltd.

Stoneware Centrifugal Pumps. It is fairly evident that, with the construction materials available, centrifugal pumps offer the best solution up to the present of the problem of pumping nitric acid. They can be readily constructed without valves and rubbing surfaces and can be made to operate efficiently at widely varying pressures.

The use of stoneware for these pumps is beset again with many difficulties peculiar to the material. For example, the body of such pumps has to be made very thick to withstand ordinary pressures, and is usually reinforced with cast iron for work at higher pressures. The impellers of these pumps are also liable to fly when rotating at high speeds. A third, and possibly the greatest difficulty, which is not limited to stoneware pumps, lies in the leakage of acid at the gland, causing

loss in efficiency and corrosion of external metal parts of the apparatus. In spite of these difficulties, however, the use of the stoneware centrifugal pump has persisted to an appreciable

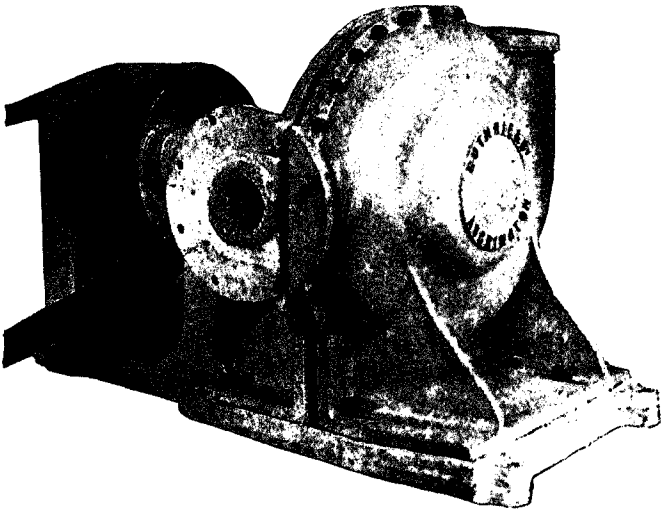


FIG. 96.—Armoured Ceratherm Centrifugal Pump.

DropBooks

extent in the nitric acid industry, mainly owing to the fact that good stoneware is almost perfectly resistant to the action of nitric acid of all concentrations. The technique of manufacture of the stoneware pumps has been enormously improved in this country in recent years, and a pump is now on the market which can be run safely at 1,500 revolutions per minute, and is tested up to 3,000 revolutions per minute. Perhaps the best-known stoneware centrifugal is shown in Fig. 96. These pumps are constructed of an acid-resisting stoneware called ceratherm. The impellers are of special design, calculated to give very little thrust along the shaft. The impeller (Fig. 97) is screwed on a steel shaft coated with an acid-proof cement. The ceratherm in these pumps is 2–2½ inches thick and set in iron casings in order to give a body

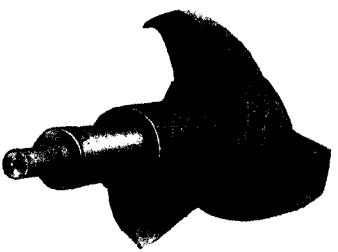


FIG. 97.—Ceratherm Impeller for Armoured Centrifugal Pump. Guthrie & Co.

which will withstand relatively high pressures. Under the most favourable conditions, with a single-stage pump, efficiencies as high as 60 per cent. have been attained with about 40 feet head. The following table will give some idea of the efficiencies attained under varying heads :—

TABLE 32

Revs. per Min.	Head in Feet.	Quantity pumped in Gals. per Min.	H.P.	Efficiency per cent.
1,750	116	160	13¼	43
1,400	87	110	6	48·3
1,750	128	120	12¼	38
1,000	35	160	2¾	62
1,665	35	150	2¼	71
1,450	35	100	1¾	60

With increase in the quantity of liquid to be pumped, the efficiency in general is increased. When it is remembered that the general efficiency of centrifugal pumps, of pumping capacity lower than 250 gallons per minute, is not more than 55 per cent., it is clear that the stoneware pumps are well up to the average, while being quite acid-resisting.

The general specification of these pumps covers a capacity from 20–500 gallons per minute, at working heads up to 170 feet,

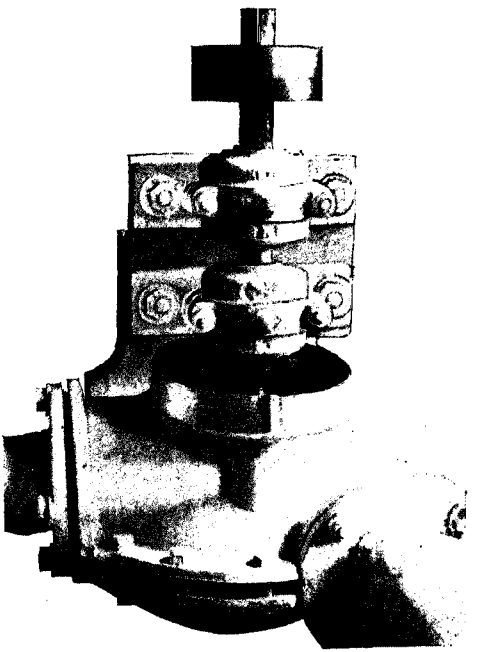
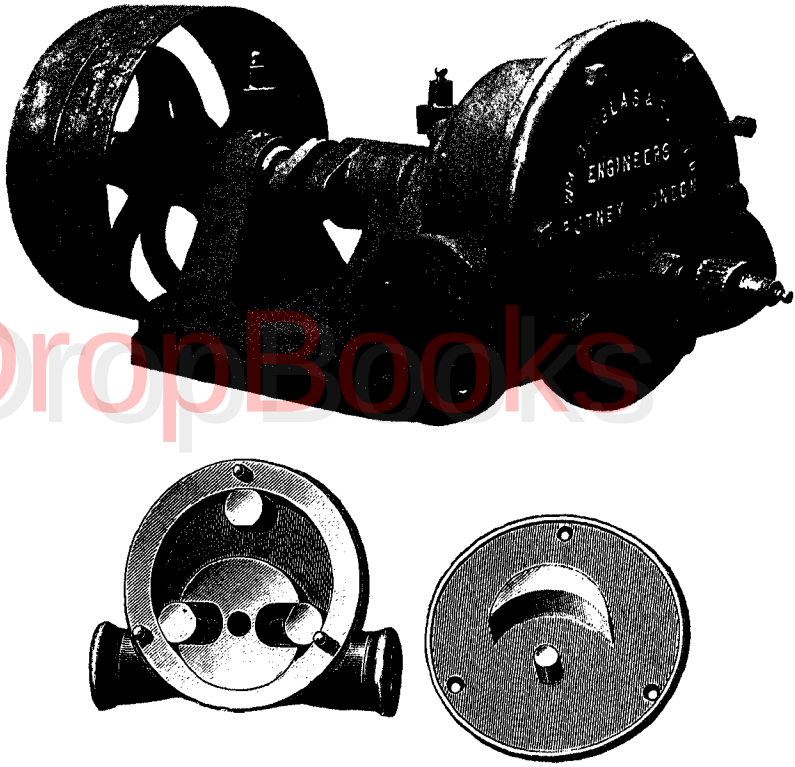


FIG. 98.—Reinforced Ceramic Pump fixed for Horizontal Work.

Guthrie & Co.

the revolutions per minute varying between 500–1,750. The pumps are also useful for hot acids, and can be used, if required, in the horizontal position. Fig. 98 illustrates the method of arrangement in this latter case. The horizontal method of operation can often be used advantageously from low-level supplies, for long-distance horizontal transit.



DropBooks

Fig. 99.—Douglas Pump.

Metal Centrifugal Pumps. Each firm manufacturing acid-resisting iron, both in this country and abroad, has marketed a pump for corrosive acids, including dilute nitric acid. In addition, there are several other firms, not makers of the material, who have produced pumps of special design for acid work. A comparison of the relative merits of these pumps is somewhat difficult, as it cannot be said that any one

of them has had a sufficient trial to establish its position finally in chemical industry. So far as pumps for strong acids are concerned, i.e. which can be constructed of ordinary cast iron, one of the outstanding pumps of recent years is the Douglas pump shown in Fig. 99. These are concentric, positive-acting rotary pumps, and are, in the author's experience, one of the most reliable pumps on the market for acid work, particularly for sludges and gritty or dirty liquids.

Another type of pump, made by Messrs. Marcus Allen & Sons, Manchester, is illustrated in Fig. 100. This is a centri-

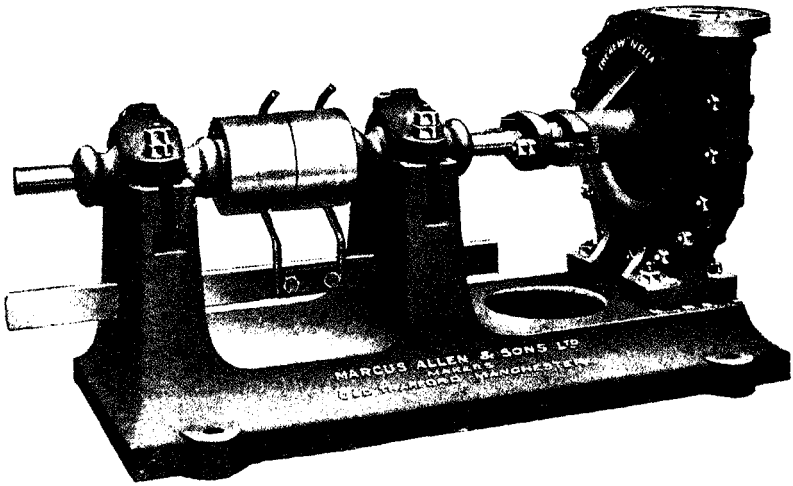


Fig. 100.—Metal Centrifugal Pump.

fugal pump giving relatively high efficiencies with dilute acids. For strong acids they are made in iron, and for resisting dilute acids in silicon-fluxed regulus metal. A particularly ingenious method of overcoming trouble due to gland leakage, etc., is illustrated by the pump shown in Fig. 101. This is a glandless, vertical-spindle, centrifugal pump. The renewal of glands and stuffing boxes is consequently eliminated, and the pump solves one of the great difficulties in the pumping of acids, viz. the securing of tight glands during pumping operations.

The commonest type of silicon-iron pump is the centrifugal. When lifting aqueous liquids the centrifugal pump gives remarkably high efficiencies, but when used for acids, difficulty

is almost invariably experienced with leaking glands, which difficulty is increased by the fact that the leaking acid attacks the bearings and journals. While the very high efficiencies obtainable with water have not been realized in chemical practice, it must be admitted that the centrifugal pump is probably the most efficient means available at the present time for elevating acids when large quantities have to be pumped, and consequently pumps of large capacity can be installed. For the smaller quantities usually obtaining in chemical practice, the efficiency of the centrifugal is somewhat lower, but still exceeds that of compressed-air elevating systems, being usually more than double.

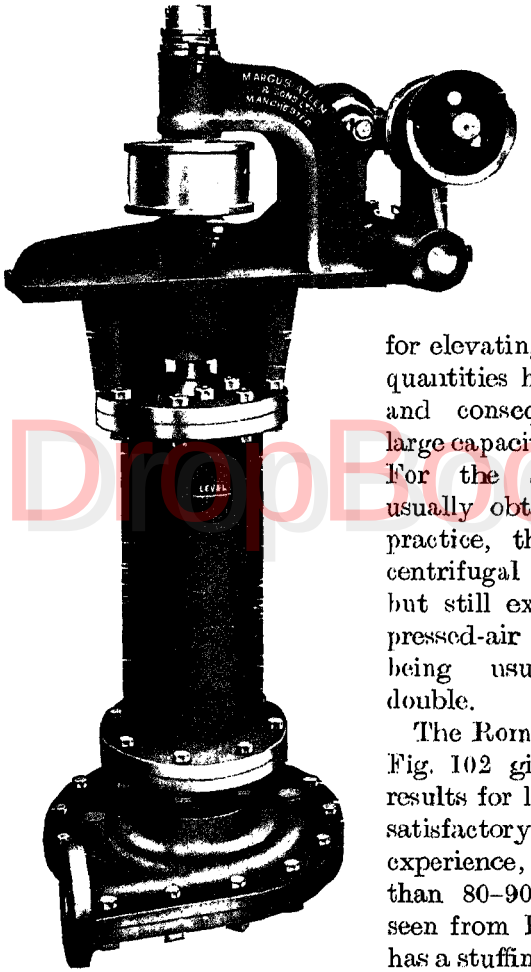


FIG. 101.—Vertical-spindle Centrifugal Pump.

The Romnic pump shown in Fig. 102 gives fairly efficient results for low lifts, but is not satisfactory, in the author's experience, for lifts greater than 80–90 feet. As will be seen from Fig. 102, the pump has a stuffing box of large proportions, the shaft being fitted with thrust and running ball bearings. All parts of the pump coming in contact with acids are of narki metal.

Messrs. Haughtons, Ltd., London, also market a centrifugal pump in their iron-silicon alloy, ironac, both one and two stage

pumps being manufactured. Similar pumps are also made by the Lennox Foundry Co. in tantiron (Fig. 103). These pumps have capacities from 60–10,000 gallons per hour and

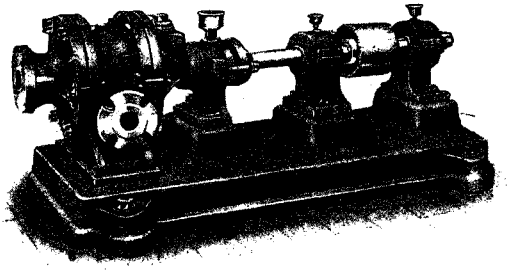


Fig. 102.—Romnie Centrifugal Pump.
John Varley & Co., Ltd.

operate at pressures up to 75 lb. per square inch. There is no doubt that the silicon-iron centrifugal pump has a useful sphere

pumps of the original Dehne type now being operated in the nitrogen-fixation industries. They have been replaced by the more modern centrifugal pump in acid-resisting metal, or else suitable types of air-elevating apparatus. There should be mentioned in this connection, however, the patent of Ferraris,[1] who interposes a layer of mercury, or some suitable oil, between the pump piston and the acid, which protects the piston from corrosion. Although the pumps designed on this principle are efficient so far as the pumping of acids is concerned, the author's experience with them up to the present has indicated that the use of a buffer layer of oil is a source of difficulty and possibly of danger in the case of the pumping of concentrated nitric acids or nitrating mixtures.

Compressed Air Apparatus

The question of efficiency is not, however, the most important consideration, at the present time, in considering the type of elevating system for dilute acids. The conditions under which plant has to be operated, in most chemical industries, are so severe, that reliability and low maintenance costs are the first essentials in equipment required by the chemical manufacturer. For this reason the use of compressed air, either in simple blow-eggs, Pohle lifts, or automatic elevators, has become almost the standard method of operation in the acid industry. While the efficiencies obtained are admittedly low, the greater reliability usually obtained with such apparatus, the mobility of air as a source of power, and the low maintenance cost of most forms of such apparatus, have caused a very wide use of air elevation systems.

Simple Blow-eggs. The blow-egg consists ordinarily of a vessel which will withstand high pressures (up to 100 lb. square inch), provided with an inlet pipe for acid and an exit pipe dipping to the bottom for the removal of the acid, and an inlet pipe for compressed air and a blow-off valve for releasing air pressure. The cast-iron egg, which is in such wide use for sulphuric acid, is not available for dilute nitric acid unless lined with some form of acid-resisting material. In some cases where very high pressures have to be used, and

[1] Eng. Pat. 4,482, 1914.

where, in consequence, the use of iron-silicon alloys is unsafe, it is the practice to line cast-iron eggs with acid-resisting tiles. Fig. 104 shows an example of such a blowing egg, which is made of cast iron and lined with acid-resisting tiles set in acid-proof cement. It operates without trouble at a pressure of 60 lb. per square inch.

Such eggs have the theoretical advantage that they are resistant to dilute or concentrated mineral acids, and should have a long life. It is well known in practice, however, that it is very difficult to line cast-iron vessels with tiles in such a

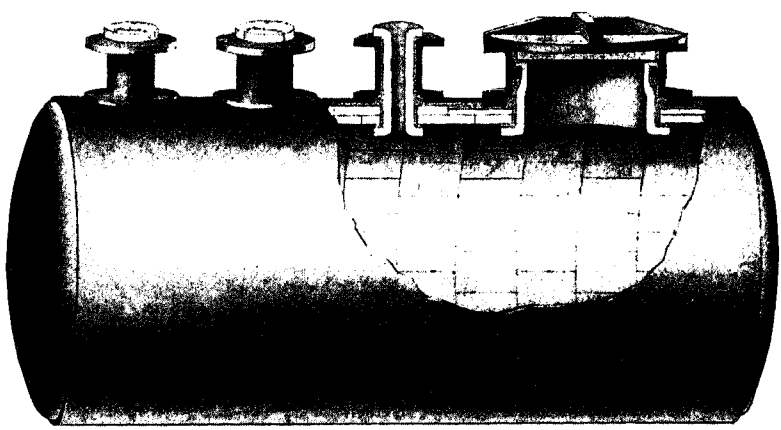


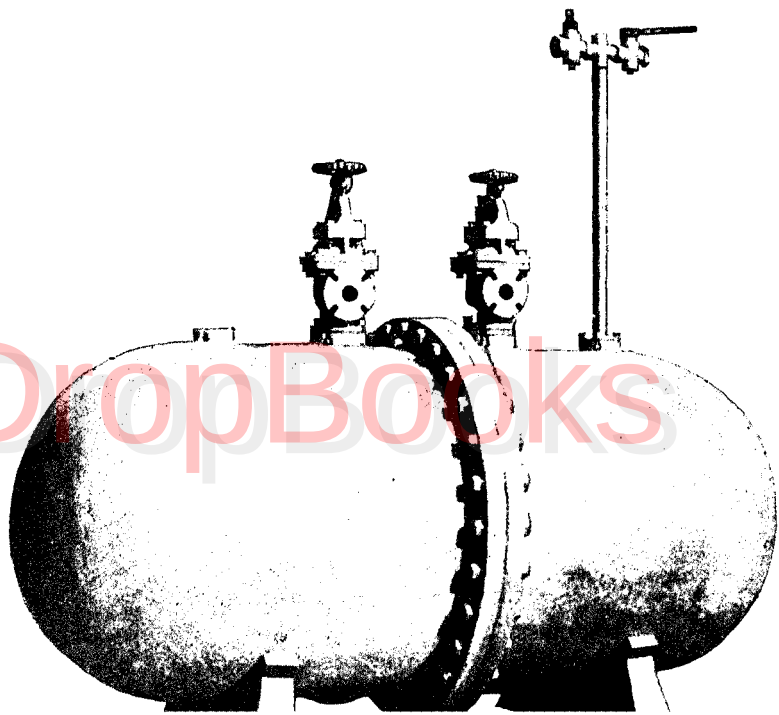
FIG. 104.—Cast-iron Blowing Egg lined with Acid-proof Tiles.
Guthrie & Co.

way that the lining is quite impervious to acids, the greatest trouble occurring with the acid-proof cement, which cracks on setting. This difficulty is being ingeniously overcome by applying a continuous pressure to the joints during the setting of the cement, so that the excessive contraction of most acid-proof cements can be compensated before the material becomes too hard. If linings of acid-proof tiles can be obtained which will remain absolutely impervious to acid under pressure, this type of construction will undoubtedly prove a serious rival to the use of iron-silicon alloys.

So far as the use of iron-silicon alloys for blowing eggs is concerned, the constructional limitations of the metal render it necessary to make eggs of larger sizes in two or more parts

with flanged joints, which latter are a possible source of weakness. The blowing egg shown in Fig. 105 is a typical example of such constructions. The central joint is made with asbestos and sodium silicate and the outside of the joint then filled with hammered lead wool.

Blowing eggs are usually laid horizontally in a suitable



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the egg were at ground level. The eggs employed for raising acids usually have capacities up to 1,000 gallons and weigh approximately 3 tons, though for the circulation of acid liquors round absorption towers, a capacity of 50–100 gallons is sufficient, provided that the blowing egg is automatic.

It is necessary to supply compressed air to a blowing egg at a pressure appreciably higher than that corresponding to the height to which the acid is to be raised, owing to the loss

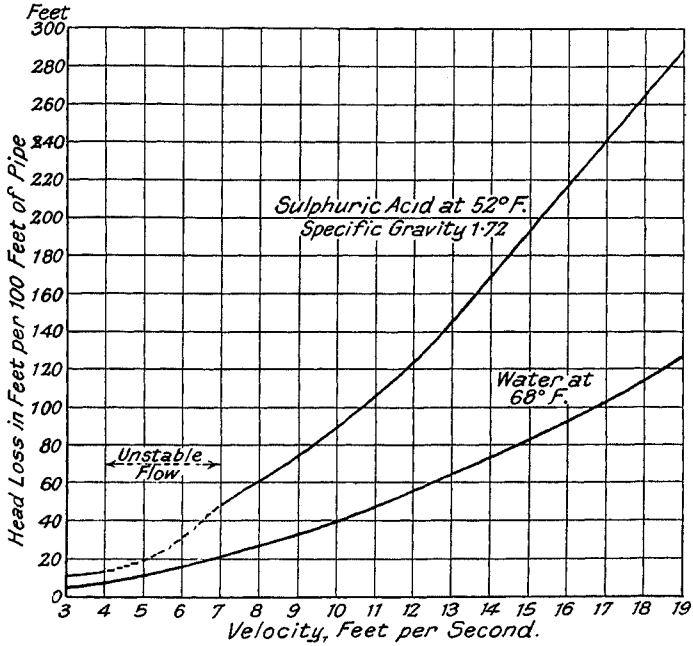

FIG. 106.—Comparative Head Loss in 1-inch-diameter Pipe.
Kestner, Ltd.

in head caused by friction in the pipe. The actual loss in head occurring varies with the diameter of the pipe and with the viscosity of the liquid being blown. In the case of a liquid such as sulphuric acid, this factor is of considerable importance. The comparative head loss in a 1-inch pipe, of sulphuric acid and water, is shown in Fig. 106 and illustrates very clearly how important this factor is in the circulation of acid liquids through pipes of small bore. Since a similar effect is also

produced on the compressed air itself, it is clear that this factor is a contributory cause to the low efficiencies obtained with compressed-air circulating systems.

The use of blowing eggs, therefore, necessitates the use of air at fairly high pressures. In the operation of such apparatus also, it is invariably the case that as soon as all the acid has been expelled from the egg, it is followed by a large volume of compressed air, varying in quantity with the skill and attention of the operator. It is evident that at least one man is required to superintend the blowing of acid by an ordinary blowing egg. As is well known, the procedure is to allow the vessel to fill with acid, and, after suitable valve manipulation, to wait until the pressure gauge shows the fall in air pressure when all the acid has been blown out. The air is then shut off, and the excess pressure blown off from the tank. The acid egg is simple and reliable in operation, and while its efficiency is very low its greatest defect is in the cost of labour in operating it. For this reason automatic elevators are usually substituted wherever a continuous supply of liquor is required, which is particularly the case in absorption systems.

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Automatic Elevators

The best-known types of automatic apparatus for elevating acids are the Kestner elevators, constructed in stoneware acid-proof metal, or in cast iron lined with acid-proof material. The general action of these elevators is illustrated in Fig. 107, showing the three stages of operation of an apparatus of the intermittent type. In the left-hand figure the body of the elevator has just filled with acid, and raised the float, which is connected by a wire to a lever in the elevator head, and balanced by an external weight. The valve admitting compressed air is just opening. When the air pressure in the body increases to a certain minimum, the acid-inlet valve is mechanically closed, and acid is forced up the exit pipe until the whole of it is expelled, provided that the initial pressure of the compressed air is sufficient. As the final volume of acid is blown out of the pipe, followed by compressed air, the pressure inside the body of the elevator drops to atmospheric, the float falls and automatically closes the air inlet and opens

the exhaust. The head of acid in the supply tank then opens the acid-inlet valve and the cycle is repeated.

A type of elevator for continuous delivery is shown in Fig. 108. The lower portion consists of two bodies, one of which

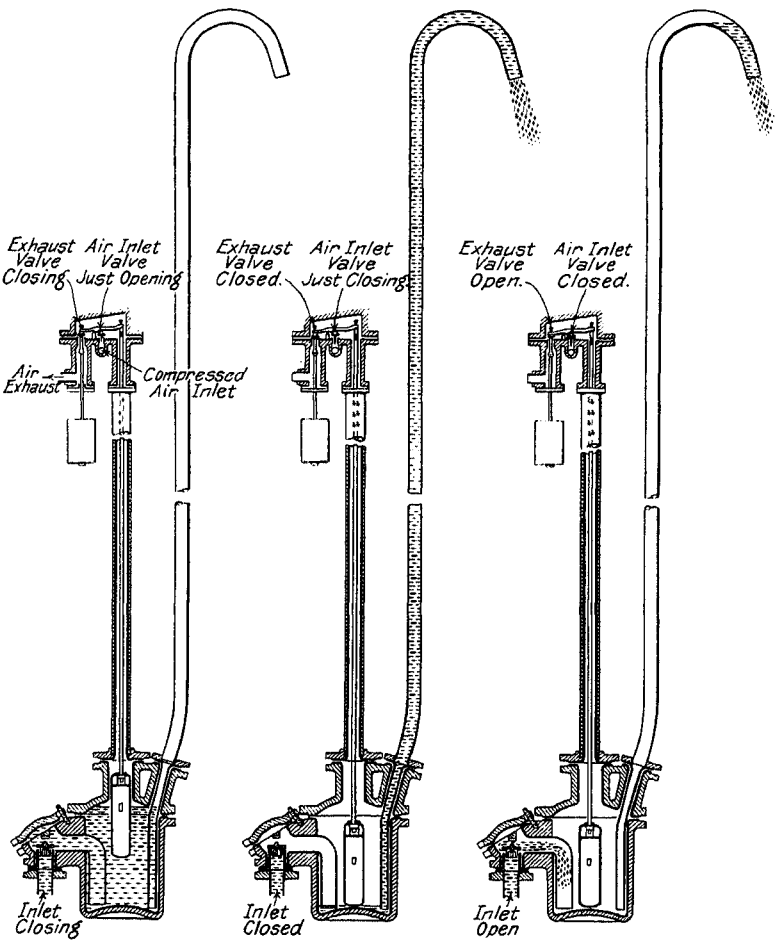

FIG. 107.—Operation of Kestner Elevator.

is slightly larger than the other to contain the float, which latter is operated by means of a simple valve. The rise of the float as the one cylinder fills operates a toothed wheel, which causes the outside weight to fall quickly. This weight in

falling turns the air on to the cylinder which has just filled, and shuts it off from the one which has just emptied, exhausting this to atmosphere.

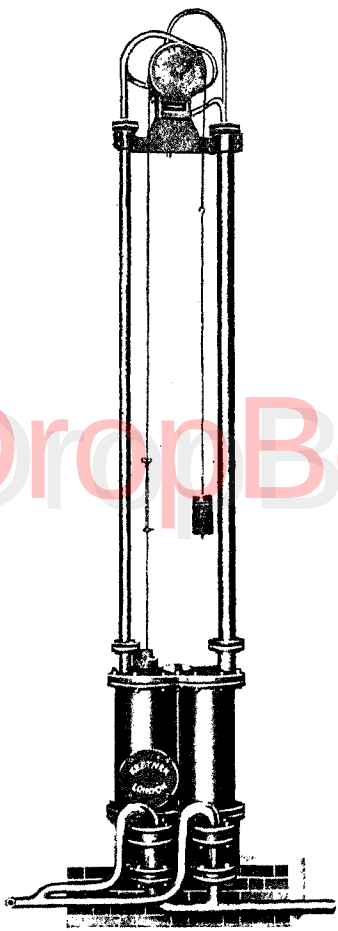

Fig. 108.—Kestner Continuous Elevator.

For nitric acid work these elevators are usually made in stoneware, and although ingeniously designed they are subject to the many deficiencies attending the use of this material in chemical industry. The bodies and flanges are made very stout in order to minimize fragility, and in this respect the construction of the flanges in the elevator shown in Fig. 109 should be particularly noted. It is important, however, in the fitting up of such apparatus that only experienced fitters should be allowed to do the work. The drawing together of stoneware flanges by bolted collars is a fruitful source of damage, as it is quite a delicate operation to secure pressure-tight joints with stoneware flanges. If the flanges are drawn up unevenly, or too tightly, a breakage results, with the consequent renewal of the elevator parts, or possibly of the whole elevator body. The position of the balance weight is also a source of danger, as the corrosion and breakage of the connecting wire may mean the fracture of the elevator body. Trouble is sometimes experienced also in the sticking of valves, particularly in the elevator head, due to the presence of

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grit on the seatings. It is therefore advisable to cover in the elevator body completely by a wooden framework. By paying careful attention to the erection of these elevators, and

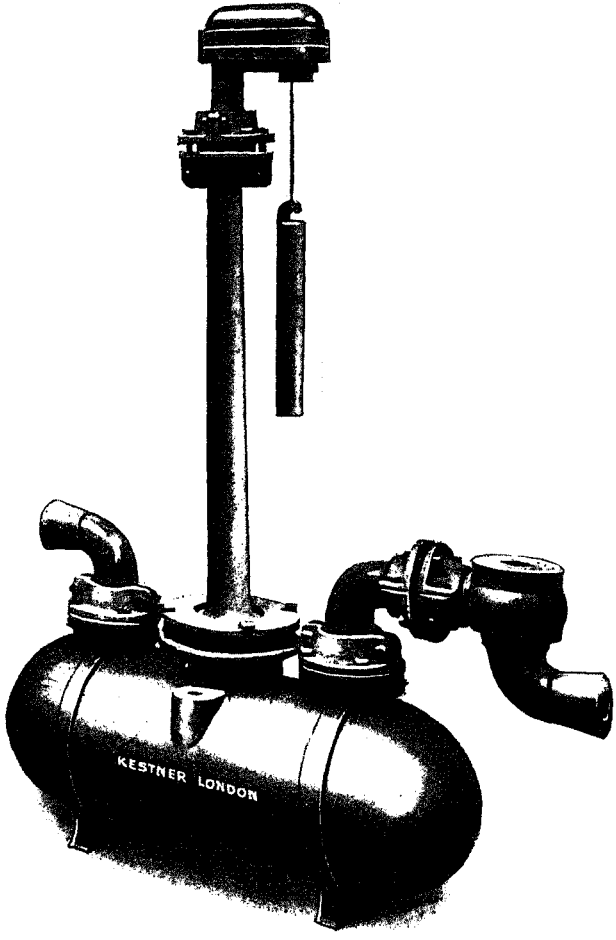

FIG. 109.—Kestner Stoneware Patent Nitric Acid Elevator.

periodic cleaning of the elevator head, these elevators can be made to give quite satisfactory service for nitric acid work.

Automatic elevators in acid-resisting iron have also been put on the market, of which by far the best, in the author's

experience, is the narki elevator, made by Varley & Co., Manchester. This elevator has been used to circulate weak nitric acid round absorption towers 50–70 feet in height connected to an ammonia-oxidation plant, and was very satisfactory although the accumulation of grit in the system caused trouble with the float and the inlet valve. The mechanism of the elevator will be evident from the diagram. The float spindle is set in the section E and operates a rocker arm in D

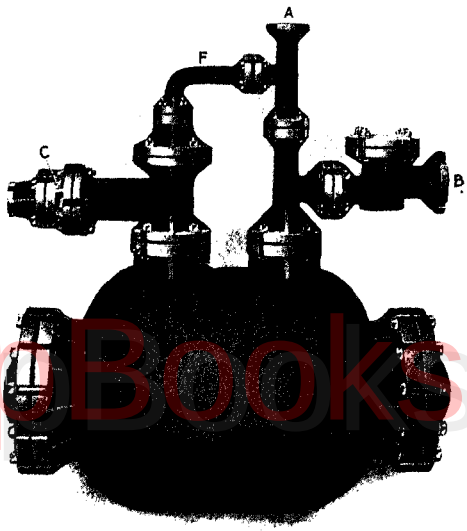

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FIG. 110.—Narki Automatic Elevator.
John Varley & Co., Ltd.

which automatically opens and closes the air-inlet valve C. The acid runs into the elevator at B, and through the non-return valve H into the body of the elevator. The float in E is lifted by the acid when a suitable level is attained, and operates the rocker arm so that compressed air is admitted and the acid is blown up the delivery pipe A.

A new and ingenious apparatus for elevating acid by compressed air is the Sullivan displacement pump, which is similar in principle to the automatic elevators previously described,

but tends to eliminate trouble due to contact of dirty acid with floats, etc. An operating model of the pump is shown in Fig. 111. It consists of two cylinders or tanks, side by side, with a common inlet and a common discharge opening, each provided with check valves. The tanks fill by gravity, and are alternately emptied of their contents by direct air pressure, which carries the liquid being pumped to the desired elevation. The filling and emptying of the tanks is controlled by an automatic switch, which is placed above the level of the acid and operated by air from a line independent of that which supplies the tanks. The operation of the switch, by alternately admitting compressed air to each tank, secures a continuous discharge of acid into the storage tank. By means of a single adjustment, made by turning a control valve, the suction lift and capacity of the pump are varied to suit changing requirements. The advantages claimed by the makers for this elevator are as follows :—

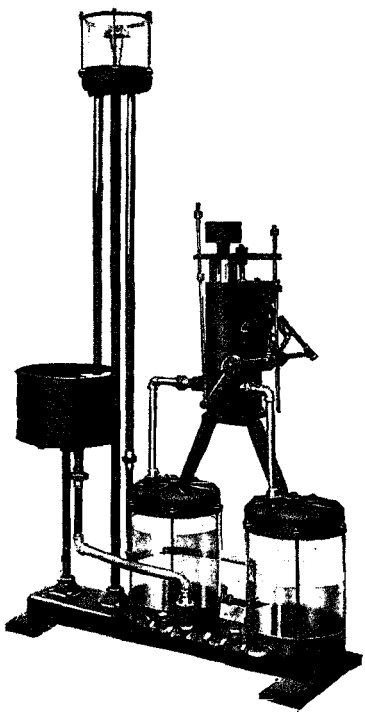

FIG. 111.—Operating Model of Sullivan Acid-displacement Pump.
Sullivan Machinery Co.

1. The liquid to be pumped does not come into contact with any moving parts, such as floats, except the inlet and discharge check valves.

2. Clearance losses are avoided, since the automatic switch leads the expanded air from the empty tank into the full cylinder before admitting live air to the latter, thus filling the lines and clearance spaces.

3. Power and time losses in overcoming inertia are obviated by this method of re-using the exhaust air, thus starting the acid before live air is admitted.

4. The speed of switching is governed effectively by an accessible valve, without other adjustment or change of parts.

5. The air pressure to the switching apparatus is regulated by an independent diaphragm reducing valve, securing positive and equal timing of the switch movement, regardless of the pressure in the air receiver.

6. There is no precipitation loss, or emulsification of the acid being pumped. The compressed air does not mingle with the liquid, but merely exerts direct pressure upon its surface.

The pump does not seem to have been used to any extent in this country, but seems to offer undoubted advantages over some of the ordinary types of automatic lifts.

The Pohle Lift.

In spite of the many advantages of automatic elevators, and the improvements in acid pumps, the fact remains that the emulseur or Pohle lift is the most reliable, and has the least maintenance cost of any method of circulating acid, in absorption towers. It is almost universally adopted, either as the sole means of liquor circulation, or as an important standby. For this reason the apparatus merits detailed consideration. The development of the air lift has been very largely connected with deep well pumping, where it is almost the only means of pumping available.

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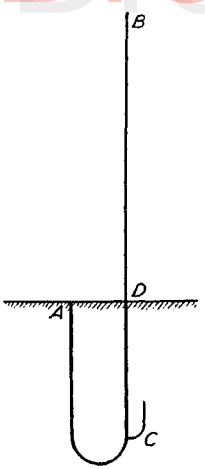

FIG. 112.

Principle of the Air Lift. The Pohle lift, as it is now called, was not invented, but only adapted by Pohle. The application of compressed air to pumping liquids seems to have been first due to Carl Löscher, in 1797. Later developments were due to Frizell in 1880 and Dr. Pohle in 1892. The principle of the air lift can be briefly described as follows :—

Consider a U tube ACDB (Fig. 112), containing a liquid able to move freely. At rest, the levels of the liquid in each arm of the U tube will be the same. If now air is introduced at C in such a way that the column BC is made to consist of alter-

nate sections of air and water, it is evident that the average specific gravity of the column will be lowered, and the liquid will hence rise to a greater height in the arm BC in order to compensate the weight of the liquid in column A.

Looked at in another way, consider a vertical pipe open at both ends, partly immersed in a liquid : normally the liquid will stand at the same height inside and outside the pipe. If now an air bubble is introduced, it will displace a certain amount of liquid in the pipe. The hydrostatic pressure on the

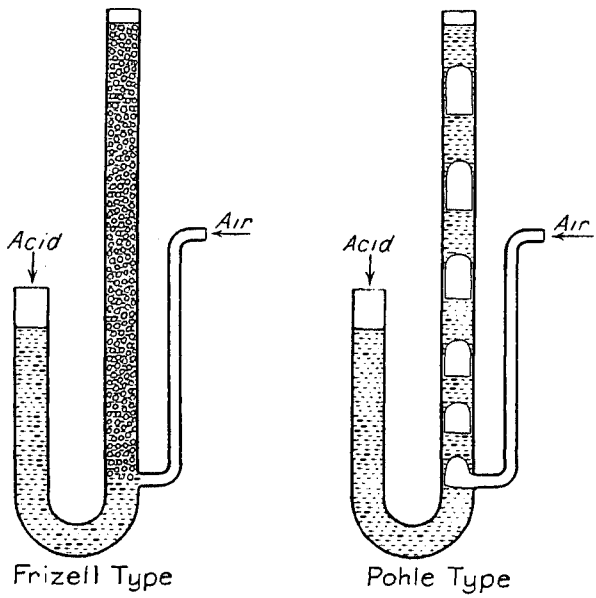

FIG. 113.—Types of Air Lifts.

underside of this bubble will now be greater than the combined weight of the liquid plus bubble, above it, and consequently the bubble and liquid above it will be pushed up the pipe until a difference in head is produced, which balances the difference between the weight of the air and the weight of the water it displaces. The introduction of more air bubbles causes the column of liquid to rise still higher, and so on. There are two methods of introducing air into the column, that is, apart from the many different types of foot-pieces which have been designed. In Pohle's type, the air is introduced as relatively

large bubbles whose horizontal width is essentially that of the pipe up which they are passing. The Frizell system is one in which a very large number of small air bubbles is introduced into the pipe, producing a type of emulsion (Fig. 113). The difference in the number and size of air bubbles introduced is produced by the use of a different type of foot-piece (see p. 256) which either allows a large number of small bubbles to pass, or else a smaller number of larger bubbles.

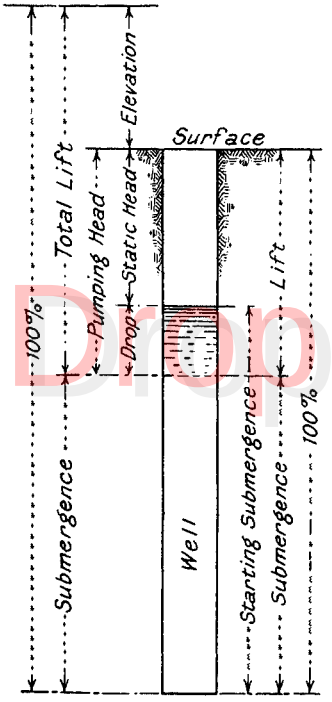

FIG. 114.—Terms used in Air-lift Pumping.
Sullivan Machinery Co.

From the description of the principle of the air lift previously given, it will be evident that to elevate a liquid from a given level A, to another level B (Fig. 112), it will be necessary to provide a fall for one arm of the U tube to some distance below the level A. The exact amount of this fall can be calculated for any given liquid, but is more easily determined by trial, in practice, as so many variables affect it. In most cases the fall below the level A is made at least one-half the height AB, i.e. one-third the total height of the longer arm of the U tube.

In Fig. 112 the fall AC is known as the "submergence," and the distance DB the "lift." The total lift plus submergence is always taken as equal to 100 per cent. Thus, if the submergence is given as 75 per cent., the lift above the surface is 25 per cent., and if the submergence is 60 per cent., the lift is 40 per cent., and so on. Thus, supposing it is required to elevate acid from ground level to 30 feet up, and it is assumed that a lift with 50 per cent. submergence would be required for this purpose, it would be necessary to sink a well for the fall tube, a distance of 30 feet.

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Where, instead of a U tube, two concentric tubes are used in a well, there are other factors which complicate the question (Fig. 114). For example, the level of acid before pumping is always higher than the level during pumping, and consequently the starting submergence is always greater than the running submergence. The "lift," in this case, is the height from the level of running submergence to ground level. The total lift is this lift plus the elevation above ground level.

For absorption-tower work there are several types of air lifts which may be used.

Well Type. This was the earliest type of lift used, and was modelled on the ordinary air-lift pump used in mining operations for elevating water. It consists essentially of a well of varying depth (12–20 feet) which is usually obtained by sinking into the ground a stoneware or acid-resisting iron pipe of 4 inches to 6 inches diameter.

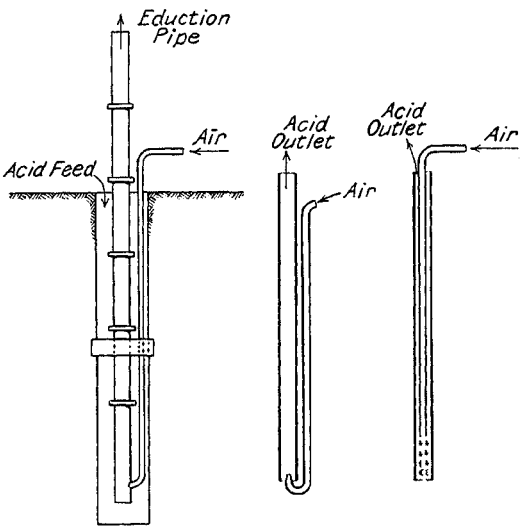

FIG. 115.—Air Lift (Well Types).

In the centre of this is fixed the lift pipe or eduction pipe, which constitutes the other arm of the U tube. A third tube, usually of $\frac{1}{2}$ inch diameter, is introduced carrying the air supply. In the commonest form, this air pipe is caused to deliver air as a jet, at the base of the inner tube (Fig. 115).

This form of apparatus may be modified in several ways. For example, the air tube may be introduced at the side of the eduction pipe, at a point about 1 foot above the bottom of the pipe. This prevents the escape of air from the eduction pipe and consequent loss of efficiency. Alternatively the air may be taken by a pipe down the centre of the eduction pipe, and escape through a number of small holes pierced in the base

of the pipe, or it may be introduced as a jet at the bottom of the eduction pipe.

The disadvantages attached to the well type of lift are as follows :—

(*a*) The long lengths of air-inlet tube required.

(*b*) The inaccessibility of the base of the delivery pipe and the air inlet, rendering it necessary to dismantle the apparatus, if adjustment or cleaning is to be carried out.

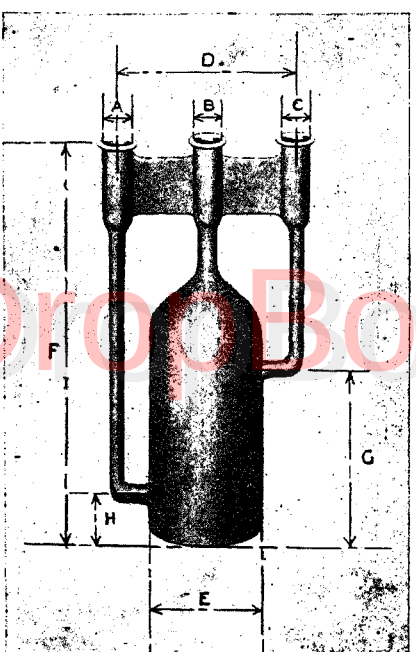

FIG. 116.—Elevator Bottle.
Oates & Green, Ltd.

(*c*) The air inlet, unless fixed to the eduction pipe, is liable to move with respect to the latter, and the efficiency of the lift is greatly impaired.

(*d*) The well tends to accumulate grit and dirt, which ultimately cause a temporary stoppage in the apparatus.

The U-type Pohle Lift. This lift does not differ at all in principle from the well type, except that the acid-inlet pipe, the eduction pipe, and air-inlet pipe, are kept in a fixed position relatively to each other by the use of a foot-piece, or alternatively by making the whole apparatus in one piece. In addition a common improvement in absorption practice is to make the tubes accessible by sinking them in a sufficiently wide pit.

The simplest type of foot-piece for small absorption towers is shown in Fig. 116, and is usually constructed in stoneware. It is also possible to make a very simple type of lift in glassware. This has the serious disadvantage in practice that it is liable to be fractured during working operations.

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An inspection of Fig. 116 will show clearly the principle of the foot-piece, sometimes known as the "monkey bottle." The acid-feed pipe is fitted into A. The second arm of the U tube is that fitted into the socket B, while air is introduced at C. The small reservoir of acid in the bottle enables steadier conditions of pumping to be obtained, and the emulsion of air and acid is carried steadily up the eduction pipe B, by suitable adjustment of the air pressure. This type of elevator bottle is very common on the small stoneware absorption towers used in this country.

A number of types of foot-piece made by the Sullivan Machinery Co., Chicago, are shown in Fig. 117.

It will be observed that these foot-pieces operate on the Frizell rather than the Pohle system, by liberating a large number of small air bubbles, rather than single bubbles which occupy the whole of the effective diameter of the tube.

It is difficult to detect much difference in the efficiency of different types of foot-piece provided that they are constructed on a rational basis and allow free passage of air bubbles into the eduction pipe. It is interesting that continental and American practice favour the use of foot-pieces of the Frizell type, while in England the Pohle type of lift is almost universal. There seems to be very little difference between the efficiency of the two in practice, but the Frizell type has undoubted advantages when the diameter of the eduction pipe is greater than 2 inches to 3 inches. For pipes of smaller diameter than this the Pohle lift has less loss due to "slip" (the return of water downwards past the ascending air bubbles) than has the Frizell type.

A type of foot-piece operating on the Pohle principle is shown in Fig. 118 and is known as the injector type.

The practical disadvantages found with the injector foot-piece are mainly its cost, the increased air consumption which seems to be necessary, and the choking and throttling of the tapered air nozzle, which cannot be cleaned without dismantling part of the apparatus. It may be taken as a general rule that the use of a tapered air nozzle, in order to increase the kinetic energy of the air, will have the reverse effect to that anticipated, and will result in lower efficiencies.

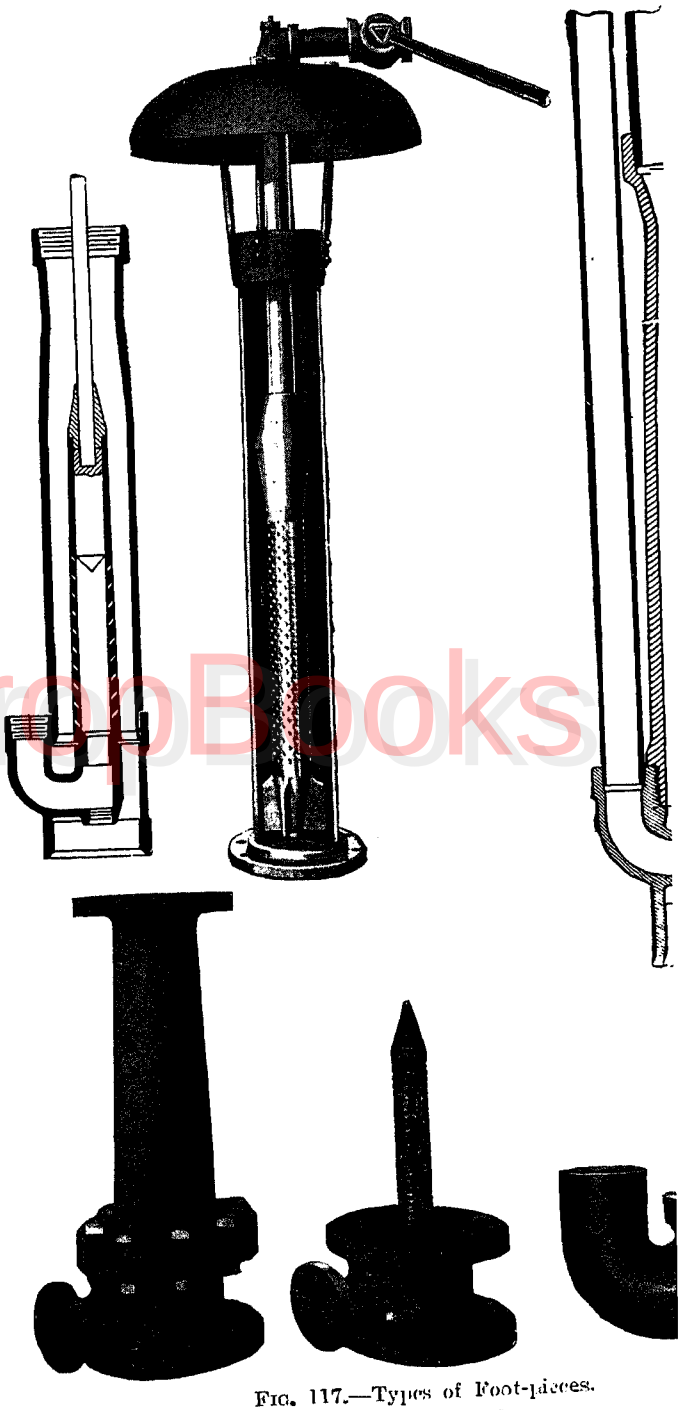


FIG. 117.—Types of Foot-pieces.
Sullivan Machinery Co.

Construction Material. In the smaller type of absorption tower, the air lifts are often made of glass pipes, 1 inch diameter, of the socket and spigot type. The socket should preferably be of the shape shown in Fig. 119 (A) rather than that in Fig. 119 (B), since if a soft cement is used for packing the joint, the cement is less likely to be forced out by the pressure of the air.

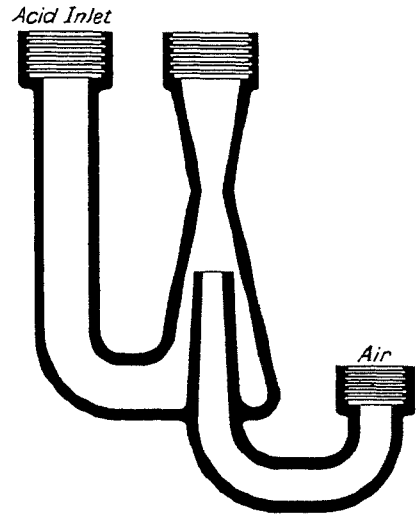


FIG. 118.—Injector-type Foot-piece.

The usual method of packing consists in coiling in a piece of ½-inch asbestos robe, and covering this with a thick putty made from linseed oil, china clay, and flock asbestos, and finally coating the outside with a mixture of plaster of paris, tar, and pitch, which serves as a protection from weather. It is

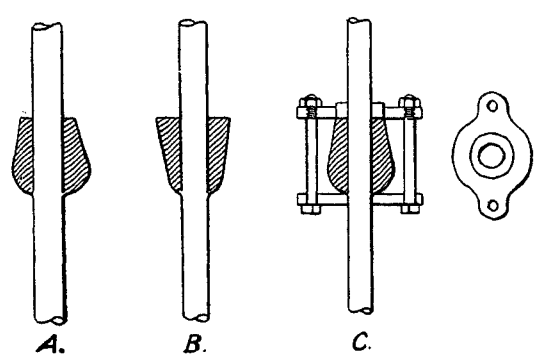
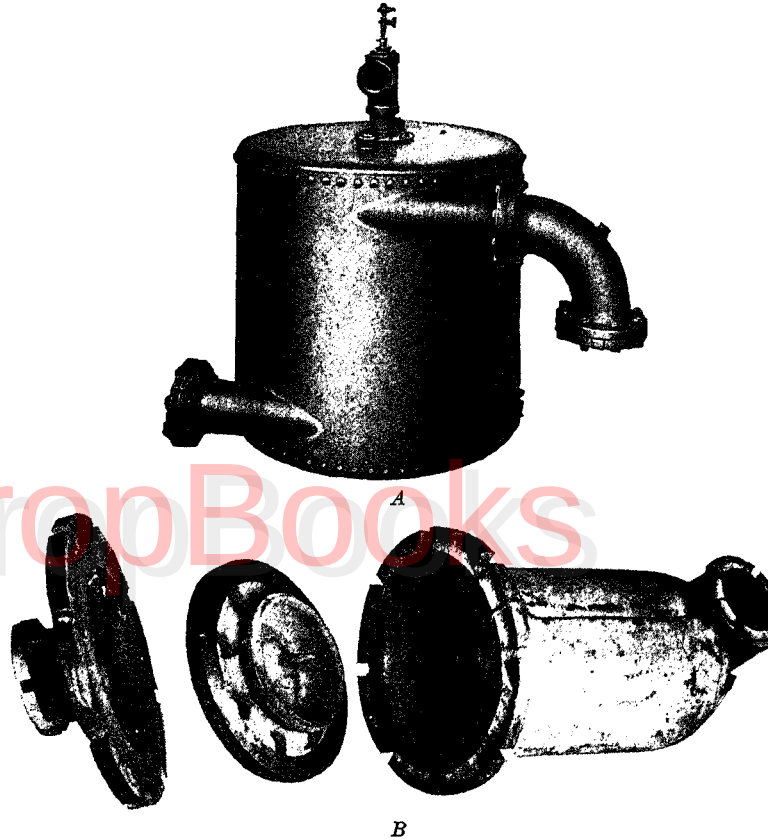


FIG. 119.—Glass Joints in Air-lift Pipes.

also advisable to fit small aluminium flanges which can be bolted to the glass cup and prevent the egress of the packing material (Fig. 119 (C)). For slightly larger towers, earthenware

pipes approximately 2 inches diameter are used, otherwise the method of construction is exactly similar.

For absorption towers varying from 40 feet to 80 feet high, it is necessary to use either acid-resisting iron, or aluminium,



A

B

FIG. 120.—Separation Heads or Splash Boxes.
A, Cast Iron. *B*, DurIron.
Sullivan Machinery Co.

as a construction material, in order to withstand the higher pressures to which the lift is subjected. Any good acid-resisting iron can be used for this purpose. In some of the earlier lifts, trouble was experienced owing to the porosity of the castings under pressure, but this has now been almost entirely eliminated. The pipe jointing used in this case consists of a

ring of asbestos board soaked in sodium silicate solution of 1·5 sp. gr., the flanges being bolted up against it, while the ring is wet.

At some of the larger nitrogen-fixation plants, aluminium pipes are commonly used for air elevation systems. They have the advantage of lightness and ease of construction, and appear to have a long life, where the nitric acid can be kept at air temperature.

Separator Heads. The nitric acid lifted is delivered at the top of the eduction pipe as an emulsion with air. In order to effect a separation of the air and acid, the mixture is delivered into a splash box, or separator head. A common type of splash box in stoneware is shown on page 160. In Fig. 120 (*A*) is shown a cast-iron separator head which can be used for non-corrosive liquids, or it may be lined with acid-resisting material for use with nitric acids. It is a convenient and compact form of separator where relatively large volumes of air have to be used. It will be observed that the emulsion of air and water is introduced tangentially, thus facilitating the separation of liquid by centrifugal action. Fig. 120 (B) shows a separator head in duriron (an American iron-silicon alloy). These separator heads were used exclusively in the air-lift installation at the Air Nitrates Plant, Muscle Shoals, Alabama (Fig. 121).

It is advantageous, though somewhat expensive, to design such separator heads with glass domes in order that the delivery of a lift can be readily inspected, since it is often the case, where a single air main supplies a number of lifts, that the distribution of air is uneven. In such cases it is often difficult to determine this fact immediately unless the delivery of each air lift can be inspected.

Efficiency of Air Lifts. It is admittedly the case that the efficiency of most air-lift systems in acid work is very low, amounting in most cases to only one-third the efficiency obtainable from a centrifugal pumping outfit. This low efficiency is due very largely to the fact that the amount of submergence which is given to the lift is relatively small, while for efficient operation a considerable percentage of the total length of the pump must be "submerged."

Davis and Weidner[1] have published a very complete investigation of the air-lift pump and established on a satisfactory basis many details of operation in air-lift pumping which have been hitherto carried out by rule-of-thumb methods, owing to lack of scientific investigation. A very

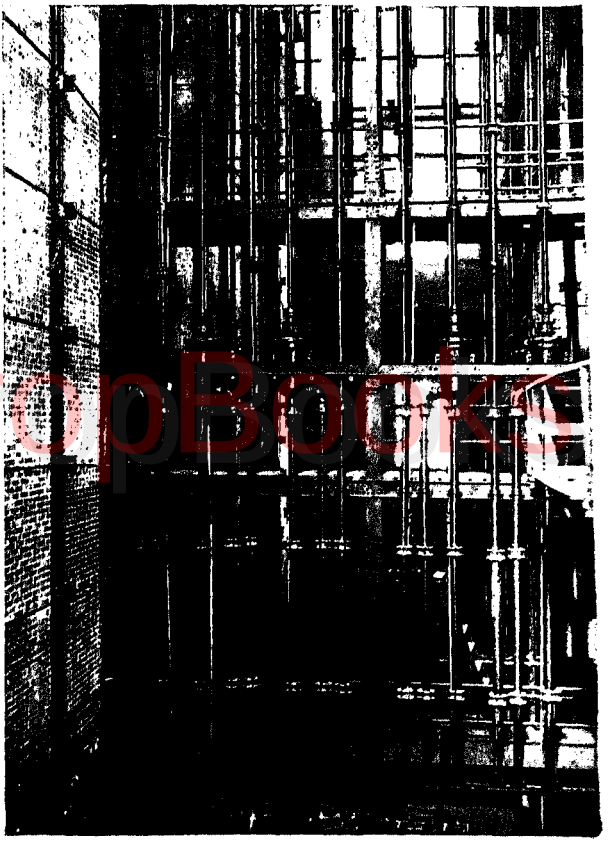


FIG. 121.—Air-lift Installation at Air Nitrates Plant, Muscle Shoals, Alabama, U.S.A.
Sullivan Machinery Co.

complete bibliography on the subject is also contained in their publication, to which the reader is referred. There are many important sets of observations in their paper, one of which has been reproduced graphically in Fig. 122. This shows the

[1] *Bull. Univ. Wisconsin, Eng. Series*, Vol. 6, No. 7, 405.

relationship between percentage submergence and the efficiency of the air lift for several different inputs of liquid, and indicates clearly that the maximum efficiency, other things being constant, is obtained with a submergence of 63 per cent. (approx.). This result is very important from a practical point of view.

An economical lift should operate at an air pressure only

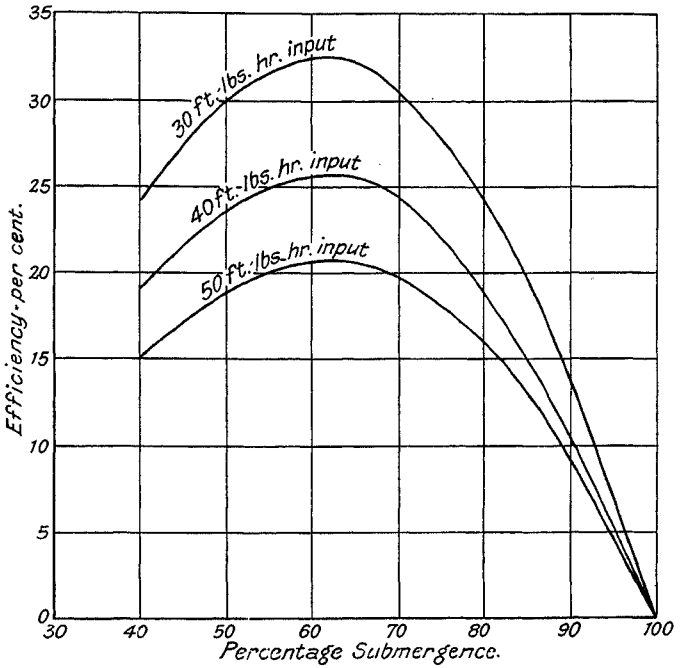


FIG. 122.—Relation between Percentage Submergence and Efficiency for Different Inputs of Liquid.

Davis & Weidner, *Bulletin Univ. of Wisconsin, Eng. Series*, Vol. 6, No. 7, 405.

slightly greater than that due to the depth of submergence, and in practice little or no advantage is gained by using pressures higher than this. It is usually taken as a practical working figure for the smaller type of lift that the volume of free air used is approximately six times the volume of acid lifted, i.e. approximately 1 cubic foot of free air per gallon of acid raised, though many air lifts consume much greater quantities than this owing to the low percentage submergence.

Though theoretical efficiencies of 70 per cent. can be obtained, the maximum efficiency generally obtained in practice is around 35 per cent. for lifts with about 60 per cent. submergence, and the efficiency falls off very rapidly with lower submergence, to figures of the order of 10 per cent. for the ordinary small-tower lifts. The percentage submergence in small absorption-tower systems is usually about 33 per cent., which means that for a lift of 12 feet above ground level, the air-lift pipe falls 6 feet below ground level.

In the case of towers 60–80 feet high, it is too costly to obtain the necessary submergence by digging pits, 30–40 feet deep, and in such cases a two-stage air lift is fitted. A good example of such was put in at the nitrate plant at Muscle Shoals, Alabama.[1] Here the acid tanks on top of the absorption towers were 60 feet above ground level, and the depth of the acid well was 20 feet. Using the 20 feet submergence, and reckoning a percentage submergence of 50 per cent., the acid was elevated to a point 20 feet above ground level. From here a new lift was started, with a total submergence of 40 feet, and, working again at a percentage submergence of 50 per cent., sufficed easily to raise the acid to the top of the tower. The two-stage lift also requires a much lower air pressure than if the lift were attempted in one stage, but, on the other hand, it causes a much larger air consumption.

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It is commonly the practice to pay too little attention to the percentage submergence of air lifts in this country. Usually the minimum submergence is used which will just allow of the elevation of acid to the height required. For this reason the efficiency of such air-lift pumping systems is invariably low, and it is not unusual to find efficiencies of the order of 5 per cent.

The work of Davis and Weidner [2] has shown a number of important points which should be borne in mind in fitting up and operating such lifts. They considered the main variables—percentage of submergence, lift discharge, volume of air, pressure of air – and their conclusions may be briefly summarized as follows :—

1. The air-lift pump with a central air tube has the greatest theoretical capacity for a given size of well.

[1] *Mines and Quarry*, Oct. 1919. [2] *l.c.*

2. The coefficient of pipe friction and slip decreases as the discharge increases, and decreases as the ratio of volume of air to volume of water increases. The term "slip" may be taken to indicate the tendency of liquid in the pipe to flow back past the air bubbles rather than be carried up above them.

3. The coefficient of pipe friction and slip varies with the length of the pump, but seems to be independent of the percentage of submergence and the lift.

4. The length of pump, the percentage of submergence (and therefore the lift) remaining constant, there is a definite quantity of air causing the maximum discharge. This quantity of air for maximum discharge, as also the ratio of volume of air to volume of water, differs for different percentages of submergence and lift, the length of the pump remaining constant.

5. The length of the pump remaining constant, the maximum output (foot-gallons) occurs at about the same percentage of submergence for all rates of air consumption, being at 61–65 per cent. for the pump used in their experiment, although the figures will probably apply equally well to all such types of pumps.

6. The length of the pump and the percentage of submergence remaining constant, and therefore the lift remaining constant, the efficiency increases as the input decreases, i.e. the highest efficiencies are obtained at the lowest rates of pumping.

7. By varying the percentage of submergence and therefore the lift, the length of the pump remaining constant, the maximum efficiency is obtained at approximately 63 per cent. submergence for all rates of input and discharge.

8. *The lift remaining constant, the efficiency increases as the percentage of submergence increases, for all rates of input and for all practical submergences.*

9. Other conditions remaining constant, there is no advantage to be gained by introducing compressed air above the surface of water in the well.

10. The type of foot-piece has very little effect on the efficiency of the pump, so long as air is introduced in an efficient manner, and the full cross-sectional area of the eduction pipe

is realized for the passage of the liquid. *Anything in the shape of a nozzle to increase the kinetic energy of the air is detrimental.*

11. A diverging outlet which will conserve the kinetic energy of the velocity head increases the efficiency.

These conclusions are very important, as suggesting the lines of improvement in the design of a pumping apparatus, which is almost universally used in the nitrogen industry.

To sum up, the main disadvantages of the air-lift pump are as follows :—

(*a*) *Low Efficiency.* This under moderately favourable conditions is only 20–30 per cent., and is usually only 5–10 per cent.

(*b*) *The Depth of Submergence Required.* For efficient results in lifting from ground level, it is necessary to carry the inlet pipe down below ground level to a considerable distance to get even moderate lifts. This can be minimized to some extent by the use of multi-stage lifts, but the expenditure of air in this case is much greater.

On the other hand, the air lift has a number of very important advantages which far outweigh its disadvantages.

1. *Reliability.* It is essential, in absorption-tower practice, that the stream of liquid down the tower should be constant in rate and unfailing in supply, and this is realized almost ideally by the air-lift pumping system.

2. *Low Maintenance Cost.* The construction of an air lift is so simple that the maintenance cost is very low, and gives to the air lift a tremendous advantage over automatic pressure elevators or pumps, in spite of the higher efficiency of these latter. The life of the air lift is almost indefinite owing to the lack of moving parts and the absence of sensitive and delicate construction. For this reason also the air lift has a great advantage over pumps, which are not normally suitable for dirty or gritty liquors which cut the packing, plungers, valves, etc. Finally the air lift is very easily dismantled and assembled.

3. *Operation Cost.* While the efficiency is low, the air pump is automatic and needs little or no attention when once started, provided that good air-reducing valves are available. Furthermore, air is a very mobile source of power and can be transmitted to different parts of the plant with relatively little loss.

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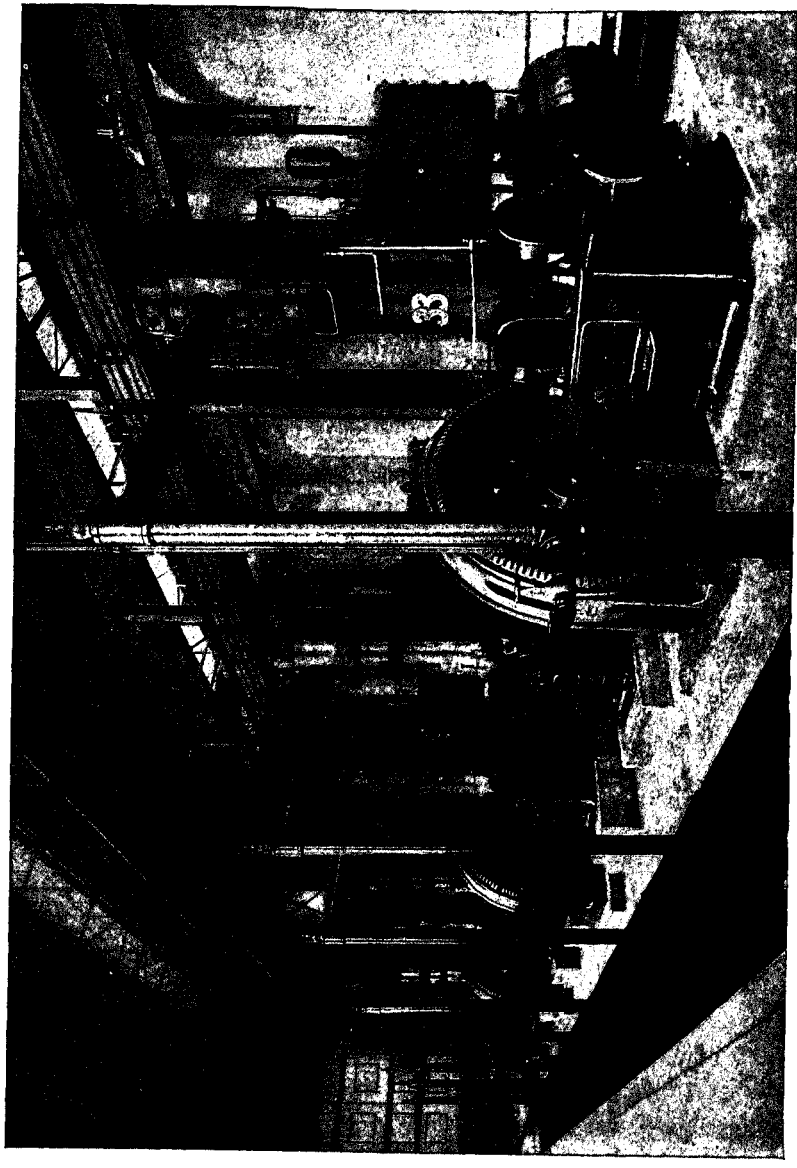

FIG. 123.—Sullivan W.N. 11-inch Twin-angle Compound Air Compressors in Plant No. 2, Air Nitrates Corporation, Muscle Shoals, Alabama, U.S.A.

4. *Temperature.* Temperature has very little effect on the air lift, and it may be used under conditions where pumps could not operate at all efficiently. It is, in fact, advantageous to heat the air used in such lifts, as the volume of free air required to elevate a given amount of acid is thereby lessened, although the rise in temperature is not advantageous from the point of view of the absorption reactions.

5. *Aeration.* It is sometimes stated as an advantage of the air lift in absorption practice that it causes aeration of the weak nitric acid and oxidizes any nitrous acid present. This latter point, however, is not the case, since no appreciable amount of oxidation can be observed during the passage of nitric acid containing small quantities of nitrous acid through an air lift. The nitrous acid is removed by the emulsification as oxides of nitrogen, which are present in such a diluted condition that their oxidation is inappreciable.

6. *Economy of Air.* The air used in such elevators may be used for the oxidation of nitric oxide in the inlet gases, where a high concentration of nitrogen oxides is being handled. The advantages of reliability and low maintenance cost are so important that the air-lift system of pumping remains at the present time the most favourable means of circulating acid which can be adopted in absorption-tower practice. In this respect the air-compression plant (Fig. 123) put down at the Air Nitrates Plant, U.S.A., to supply the air-lift pumps to the absorption towers, is significant of the present attitude of the nitrogen industry to air-lift pumping for corrosive liquids. So far as the disposition of the circulating scheme is concerned, it is the common practice and the best practice to provide each absorption tower with an independent circulating system. With the small type of stoneware tower it is also advisable that each tower should be fitted with an independent feed of water, in order that the concentrations of acid in the set of towers may be adjusted as rapidly as possible, to meet fluctuations in the supply or concentration of the oxides of nitrogen entering the system. The amount of water entering the system should also be measured. This may be done by computing the discharge of an air lift, elevator, or pump, or, where available, a graduated weir may be used with efficiency to show at a glance the amount of water entering the cycle.

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Storage of Nitric Acid

The storage of weak nitric acid in bulk is an important problem in absorption systems. It has two aspects—firstly, the storage of acid in the absorption cycle itself; and secondly, the storage of the final product—and the problem occurs with different intensity as the tower system is composed of the small stoneware towers or the much larger brick towers.

Small Absorption Towers. The elasticity of the small absorption towers, usually operated in sets of eight, is very small. As will be readily understood, the amount of actual liquid being delivered from the system is small, and in consequence, fluctuations in the water feed, or in the amount of nitrous gases passing through the system, produce rapid changes in the balance of the cycle which operate adversely on the efficiency. It is essential therefore that in each of the eight towers the amount and concentration of the absorbent delivered down each tower should be accurately adjusted, and hence that a sufficient bulk of liquid should be retained in the cycle in order that the effect of fluctuating conditions may be minimized.

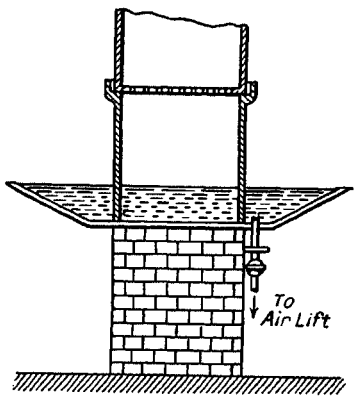

Fig. 124.—Open Saucer Storage in Towers.

The distributor or acid-receiver, placed on top of the towers, to receive the elevated acid and pass part of it on to the next tower, is usually so small that its storage capacity is negligible, and some storage for acid is usually provided at the base of the tower. In the older type of absorption system this was done by standing the tower in an open saucer which contained sufficient acid to serve as a seal (Fig. 124).

A much improved type, however, is that shown on page 163, in which the bottom section of the tower is made into a receiver and from this the acid is drawn off to the air lifts. In this way a storage of 10–20 gallons of acid may be obtained in the tower.

Thus the concentration of acid leaving a particular tower may be made approximately constant and the standard working conditions rapidly attained. It is a matter of common experience, however, that the small tower systems require constant attention to the water feed if efficient results are to be obtained, and it is an inevitable conclusion that the tower storage provided is quite inadequate. This could be improved by fixing a larger receiver on top of each tower with a storage capacity of 30–50 gallons, and also by increasing the rate of circulation of liquid in each tower, thus giving much more stable absorption conditions. It is, however, unnecessary to press this point, since the small type of stoneware tower is rapidly falling into disuse in the nitrogen industry in favour of the large-type tower of stone or acid-proof metal.

Larger Absorption Towers. With increase in the capacity of the tower and consequently in the amount of liquid to be circulated, the question of "local" storage becomes increasingly important. A single passage of sufficient liquid down such a tower as will renew the whole of the wetted surface does not generally produce a nitric acid which is of sufficient concentration to be removed from the system and used elsewhere. It is usually necessary to circulate a given volume of liquid a number of times down the tower. A considerable storage, at least at the base of the tower, must therefore be provided. A hand-to-mouth system of circulation may operate successfully for short periods, but breakdowns in pumps and elevators, etc., are very common, and in such circumstances the tower becomes water-logged and is liable to be permanently damaged. The storage provided should be in sufficient ratio to the amount of liquid being circulated to allow for a 6–12 hours stoppage, and be able to take the whole of the circulating liquid from the tower.

The storage of circulating acid on the top of such towers is not invariably practised in large-scale work. The use of various compressed-air elevators and pumps leads to the method of delivering under pressure straight down the tower, taking advantage of the pressure on the liquid to secure efficient spraying. There is undoubtedly a great deal to be said for this where the towers are not too high to prevent appreciable pressures being obtained at the top. For towers 70–80 feet

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high, however, the use of high-pressure pumps or compressed air is inadvisable, since it is difficult to obtain mains which will withstand the pressures required. For such towers the Pohle lift is most commonly used, and in consequence the liquid has no appreciable pressure at the top of the tower. In such cases it is advantageous for good working to provide suitable storage, since in this way the amount of liquid delivered down the tower may be made constant, and steady conditions of working obtained. In such a system, this provision of acid storage at the top and bottom of the tower results in a considerable saving of labour. If the top storage is made slightly larger than the storage tank at the base, the latter may be connected to the emulseurs or automatic elevators, and the acid circulated without further attention and without danger of overflows taking place.

Storage of Nitric Acid as the Finished Product. Concentrated nitric acid is not obtained directly from absorption towers, but where it is produced as a final product its storage does not present any great difficulty. It can be stored quite readily in cast-iron, wrought-iron, or even lead vessels without attack. It is necessary, however, to exclude rigidly any moisture from entering the storage vessels, or the dilution at the surface of the acid causes considerable corrosion. The addition of 5–10 per cent. of concentrated sulphuric acid renders the possibility of corrosion even more remote, and such acid may be stored in covered wrought-iron tanks for indefinite periods without trouble. The storage of weak nitric acid, however, constitutes one of the great difficulties in nitric acid production. The materials suitable for construction of storage tanks are limited, and nearly all of them have the great defect that the size of the storage vessels possible of construction is comparatively small. For small outputs of weak acid it is common practice to run out the acid from the absorption system directly into glass or stoneware carboys.

These consist of glass vessels packed in straw and encased in iron hampers. The straw is usually rendered fireproof by soaking in zinc chloride solution, or a solution of neutral sodium sulphate. These carboys are loosely plugged with a conical earthenware stopper and luted round with a soft putty made up with linseed oil, china clay, asbestos, and tallow.

The use of carboys for storage entails very heavy labour costs, and cannot be tolerated where large quantities of material have to be handled. In addition, considerable losses of nitric acid by spilling and as vapour invariably occur, since the stoppers cannot be luted tightly, owing to the decomposition of the acid effected by sunlight. As will be readily understood, the handling loss with carboys is likely to be heavy, particularly if they are used as a means of moving weak nitric acid from one part of the plant to another. In this connection it should be mentioned that there are a number of syphons, hand-pumps, etc., which can be used to facilitate the emptying

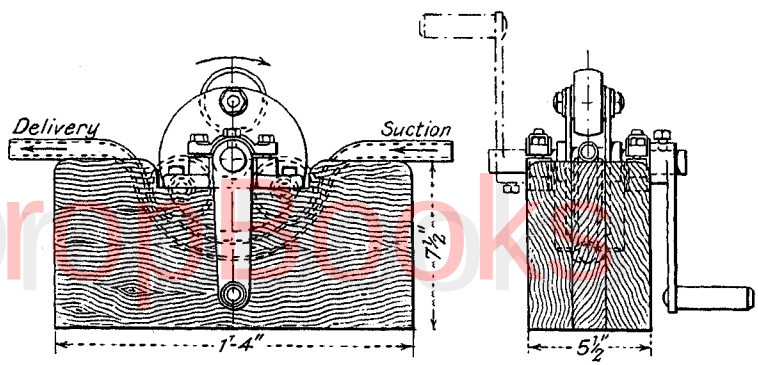

Fig. 125.—Pump for Use with Carboys.
Kestner, Ltd.

of carboys. Fig. 125 shows a convenient and useful type of hand-pump for this purpose. Except as a matter of occasional utility, however, the use of carboys for acid storage or transfer is quite uneconomical and should certainly not form a permanent part of the cycle of operations.

The commonest type of storage tank for weak nitric acid is the stoneware "bosh" (Fig. 126), the largest type of which will hold up to 500 gallons. Since in some of the larger absorption systems in Norway and America the amount of liquid circulating in the absorption towers is some 200–400 gallons per minute, the inadequacy of such vessels for use in connection with large-tower systems is quite evident.

Both slate and granite tanks of much larger capacity have been constructed for nitric acid storage, but in each case the jointing material offers considerable difficulty, since most of

the so-called acid-resisting cements are disintegrated fairly rapidly by nitric acid containing 50–60 per cent. HNO_3.

The problem has been met in America by the construction of tanks of acid-proof bricks laid with acid-proof cement. The most successful cement in this connection seems to be a "Duro" cement having a sodium silicate basis, and at the nitrate plant in Alabama tanks were successfully built having a capacity for 500 tons of weak nitric acid.

Somewhat smaller tanks on similar lines have been built in this country using acid-proof brick and a special sodium silicate cement.[1] These were made to hold 15–20 tons of dilute nitric acid, and a considerable amount of experience has been gained in the construction of such tanks, which can now be built successfully. Their use has not as yet been extensively developed in this country, but for large-scale operations they are undoubtedly a tremendous improvement on the old type of earthenware storage tank of small capacity.

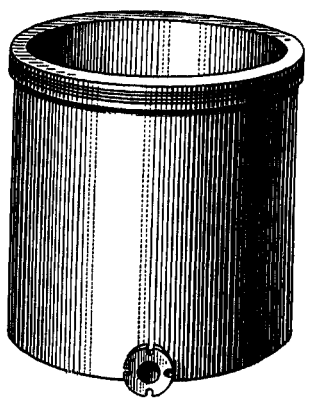

FIG. 126.—"Bosh" for Storage of Weak Nitric Acid.

It should also be mentioned that the use of cast-iron and steel tanks lined with tiles laid in acid-proof cement has also been extensively developed in recent years for nitric acid work, particularly in Germany, not so much from the point of view of storage as for reaction vessels, the contraction on setting, which is excessive with most acid-proof cements, being taken up by slow compression of the tiles during setting.

Transport of Nitric Acid. The regulations of British railways for the transport of nitric acid contain the following conditions :—

1. The acid shall be packed in sealed stoneware jars protected by wickerwork.

2. Bottles must be packed in cases or boxes, and the inter-

[1] Brit. Pat. 119,966, 1917.

stices filled with kieselguhr or some other inert absorbent material, and not with wood shavings, straw, etc.

Such regulations, of course, cannot apply seriously to large-scale manufacture of nitric acid either for home consumption or export, and, for the transport of nitric acid in bulk, use is made of the tank wagon. Here again the difficulty of a suitable construction material recurs. The usual type of wrought-iron tank may be used for nitric acid, but trouble invariably occurs owing to moisture, and the tanks corrode rapidly. This difficulty is particularly great owing to the vapour of nitric acid condensing on exposed parts of the wagon fittings, which soon become useless. The addition of 5–10 per cent. by weight of strong sulphuric acid, by lowering the vapour

FIG. 127.—Aluminium Tank Wagons for transporting Nitric Acid. Norwegian Hydro-electric Company.

pressure of the nitric acid, enables this difficulty to be overcome to some extent, but this addition is not always possible, as it depends upon the use to which the nitric acid is to be put. The use of aluminium for the construction of such tank wagons has been attended with considerable success, and the Norwegian Hydro-electric Company have a number of them in continuous service (Fig. 127).

These tank wagons require thorough cleaning after having been emptied of nitric acid. They are hence given a wash with dilute sodium carbonate solution immediately after emptying, and are then thoroughly washed out with water. In this way, corrosion of the tank, by the dilution of "films" of strong acid left in after emptying, is avoided.

The use of wrought-iron vessels lined with acid-proof tiles has also been developed for the transport of nitric acid. Here again the life of the vessel is dependent on the quality and serviceability of the acid-proof cement obtainable. Provided that this is satisfactory, there is considerable scope for such transport vessels in the industry. Tank wagons in iron-silicon alloys do not seem to have been developed successfully up to the present. The necessity for great thickness of metal, and the liability to fracture, are important factors against the use of such alloys in tank-wagon construction, where safety is essential and excessive weight undesirable.

The economic transport of nitric acid in bulk is a problem which has yet to be solved satisfactorily by the chemical engineer. Halvorsen [1] recommends the absorption of nitrous gases in concentrated sulphuric acid, and the subsequent transport by rail of the resulting nitrosyl sulphuric acid in iron or aluminium vessels. A number of other patents exist to facilitate transport of nitric acid, and many cover the absorption of the acid in various inert materials, such as kieselguhr, etc.,[2] and its subsequent regeneration by distillation or similar treatment. These methods do not commend themselves for general practice, however, for a number of reasons: Firstly, a considerable loss of valuable nitric acid always occurs on attempting to distil it away from such substances; secondly, the concentration is invariably reduced by the process of distillation; and finally, for most industrial purposes, as pure a nitric acid as possible is required, and such means of transport tend to cause an impure final product.

Acid-resisting Cements

Every plant dealing with nitric acids, either dilute or concentrated, requires jointing and luting material, capable of withstanding the action of the acid. There are many uses for such a material, e.g. jointing stoneware pipes and stoneware sections, luting in stoneware cocks, building acid-storage tanks, setting gauge glasses for storage tanks, etc., etc.

The materials used can be divided readily into two classes, (1) hard cements and (2) soft cements or putties. The type of cement used depends on a number of factors such as perma-

[1] Norwegian Pat. 15,021, 1906. [2] D.R.P. 24,748, 1910.

nence of construction, temperature to which the apparatus is subjected, etc. It is inadvisable, for example, to joint stoneware pipes of the socket and spigot type with a hard cement, if they are likely to be subjected to changes in temperature, since the expansion of the cement will usually crack off the collar of the pipe. In any case, it is almost impossible to take down pipe-lines so constructed without breaking the majority of the pipes. On the other hand, joints which have to withstand pressure must usually be made with a hard cement.

Hard Cements. As is well known, Portland cement is quite readily disintegrated by dilute or concentrated nitric acid, and, although it may be used for foundation work in many constructions, it is a potential source of danger if it is likely to come in contact with nitric acid. The behaviour of brickwork under such circumstances is well known, the "lifting" effect being so powerful as to destroy the security of any structure erected above it. For this reason ordinary cement and mortar should be used with great caution in the construction of plant for the treatment of nitric acid.

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The commonest type of hard-setting cement, which finds extensive application in acid manufacture, is a mixture of sodium silicate with various finely powdered siliceous materials. As long as it is resistant to acids, almost any type of siliceous material will do. Quartz, sand, asbestos, brick, etc., in a finely ground condition are all efficacious. The sodium silicate used in these cements should be of the non-vitreous type. As is well known, a considerable change in the properties of sodium silicate (soluble glass) occurs on heating the solution to dryness. The product becomes relatively insoluble, and cements made from it form weak, friable masses which are readily disintegrated. In this connection it should be mentioned that R. M. Caven[1] states that if a finely subdivided alkaline silicate is mixed with 25-38 per cent. of its weight of water, heated to a temperature between 70°-100° C. until the mass becomes vitreous and miscible with water and is then cooled, a hard solid is obtained, which can be ground to powder, and when stirred with water readily dissolves, only about 1·5 per cent. remaining insoluble.

[1] Eng. Pat. 106,247, 1917.

Although the use of powdered silicate in this form would offer a number of advantages in practice so far as mixing, storage, transport, etc., are concerned, the material commonly used is the ordinary viscous, liquid silicate of commerce, of approximately 1·70 sp. gr.

Cements are now on the market, however, which are supplied as a dry powder, for mixing up with water. The advantage of a single substance which will mix with water, as compared with sodium silicate, is very important in practice, but unfortunately the resulting cements are usually very poor so far as binding qualities are concerned.

Liquid sodium silicate is often used diluted to between 1·50–1·30 sp. gr. In jointing together flanged pipes of acid-resisting iron, a common device consists in soaking an asbestos washer in such silicate solution and pulling the flanges tight while the silicate is wet. A similar method is used for jointing stoneware flanged pipes. For plugging joints in acid tanks the sodium silicate solution is made into a paste with asbestos fibre and flock asbestos, and rammed in with a blunt chisel. Similarly, the blocks in absorption towers are sometimes laid with mixtures of sodium silicate solution and ground quartz or granite, which is passed through a sieve of 100–120 mesh per linear inch.

While such mixtures are useful for small constructions, they have a large number of disadvantages if an attempt is made to apply them to large-scale constructions. These disadvantages may be summed up as follows :—

1. The cements are too sticky to work with the trowel.
2. They do not possess a sufficient rate of initial set to bear the weight of the upper courses without oozing.
3. They do not possess sufficient " body " to resist sliding, and it is impossible to plumb up brickwork laid with these mixtures.
4. Their rate of setting is too slow to allow of building operations being carried on at a reasonable speed.
5. They have a relatively large expansion or contraction on setting.
6. They are apt to be disintegrated by hot water.
7. Their binding power is often relatively small.

Chance and Hunt, Holley and Webb describe a cement

which is based on the rapid acceleration of the initial set of such mixtures, by the addition of a small quantity of a salt having a catalytic effect on the setting.[1] The cements so obtained can be used with the ease and certainty of mortar for most types of construction, and have been successfully applied to the construction of brick absorption towers 70 feet high and 12 feet internal diameter, denitration towers, Gaillard towers, storage tanks, etc.

In America a similar cement has been developed, which contains finely ground quartz and an "improver" which is a calcium salt, the dry powder being made up with sodium silicate of 1·4–1·5 sp. gr. The material is sold under the name of Duro cement, and has met with extensive application in the construction of towers and acid-storage tanks. With all these silicate cements, it is an advantage to treat the exposed surface of the cement, when laid between the bricks, with concentrated sulphuric acid, which causes the deposition of a protecting film of silica on the surface of the joint.

In contact with hot and very dilute acids, these silicate cements are liable to disintegrate unless very carefully dried. In contact with concentrated acids, they are usually very durable. The drying should preferably be by use of external heat at temperatures of 100°–200° C., as the sodium silicate hardens only very slowly in air, and the rate of hardening appears to be retarded by the presence of carbonates *in situ*.

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Gauge Glasses. The use of gauge glasses in acid manufacture still obtains, although fraught with considerable danger. A cement which will adhere to both glass and metal, and which will set to a hard, resistant mass, is made by mixing red lead and glycerine to a smooth paste, which dries to a hard mass in 12–15 hours, and will then resist weak or concentrated nitric acid or mixed acid for long periods.

Stoneware Pipe-lines. Where a pipe-run is to be laid for conveying nitrous gases which are at a fairly constant cool temperature, the joints are often filled with a hard cement, in order to avoid the necessity for supervision and renewal which the use of a soft putty entails.

A hard cement for this purpose is made by melting up roll

[1] Eng. Pat. 110,258, 119,956, 1917; U.S. Pat. 189,668, 1917.

ır and mixing it with about one-third its weight of fine
The mixture is run while molten into the socket joint
lowed to solidify, when it forms a hard, resistant mass.
res of sodium silicate and ground quartz, etc., should
› used for stoneware pipe-lines, as the results are never
ctory owing to cracking, separation from smooth
es, etc.

t **Cements.** The use of soft cements or putties has
advantages for some types of acid plant: in particular,
neware pipe-lines where extreme changes of temperature
ely to occur, for luting stoneware taps, and for rendering
and joints approximately gas-tight. The ordinary type
ture for this purpose consists in incorporating a drying
h materials such as asbestos, china clay, tallow, etc. A
on mixture contains, for example, linseed oil, china clay,
os fibre, and tallow. Such a putty is not, of course,
y resistant to nitric acids. An increase in the tempera-
f the acid will cause a certain amount of nitration of the
tuent oil. The area of the cement exposed to the action
acid is normally so small, however, and the renewal of
inting material such an easy matter, that a soft cement
, comparatively short life is preferable to a hard cement
, while being more resistant, causes a great deal of
e in cracking. It will be evident that the extensive use
h a putty in a pipe-run conveying hot concentrated
acid will tend to cause the formation of nitrous acid
to the oxidation of the oil present, and this point should
efully watched if " bleached " nitric acid is being handled.
n advantage in the case of this putty to omit the tallow
ıter resistance to acids is required.

er soft putties can be made up by the use of varying
tions of tar and pitch, to which is usually added about
cent. of plaster of paris or barium sulphate. The func-
f this latter material is very indefinite. In fact, it could
ly be replaced by any finely powdered, slightly hygro-
material. Bitumastic compositions and asphalts are
sed largely for resisting cold dilute nitric acid, but these
adily attacked if a rise in temperature occurs. The
has found very wide differences in the resistance of
ts to nitric acid, and the only present method of com-

parison seems to be in making actual nitration tests on all materials before putting them into commission.

There is still a great need in chemical industry for a good acid-proof putty and also for a cheap acid-resisting cement. The development of such materials will inevitably lead to an enormous and important series of economies in present-day plant construction.

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CHAPTER VII

PRODUCTION OF CONCENTRATED NITRIC ACID

The market for the dilute nitric acid which is the normal product of the absorption of nitrous gases by water is very small, and the handling and transport of the product difficult and costly. It is necessary, therefore, to find some commercial outlet for the product.

Technical Utilization of Weak Nitric Acid. The method of utilizing weak nitric acid commercially will naturally depend on the quantity produced and whether or not it is the main product of the factory. For small productions of the acid as a by-product in a cycle of operations, the technical utilization is fairly simple. A certain amount of such acid can be absorbed in Chamber sets for sulphuric acid manufacture, and the Öpl plant is particularly suited for its introduction.

It is well known also that the sulphuric acid used for the manufacture of nitric acid from sodium nitrate should contain 90–92 per cent. H_2SO_4. It is possible therefore to use 95–96 per cent. H_2SO_4 in such nitric acid plants, and obtain the necessary dilution by the addition of weak nitric acid to the still. In this way a certain amount of the nitrous gases from a nitric acid plant may be re-absorbed into the cycle and converted to concentrated nitric acid. Normally about 5 per cent. of the total nitrogen in such plants is recovered as weak acid from the absorption towers, and it can readily be shown that using 96 per cent. H_2SO_4 in the stills and adding weak nitric acid to cause a dilution to 90 per cent. H_2SO_4 would enable twice the amount of dilute nitric acid actually produced to be absorbed.

Dilute nitric acid may also be incorporated in mixed acids, provided that sufficient oleum is available to take up the excess water (if ordinary nitrating mixtures are being produced). This method is wasteful, however, and tends to cause excessive

amounts of sulphuric acid in the plant cycle. A small amount of such acid is also used in this country for the production of ammonium nitrate and metallic nitrates.

Where the main product of the cycle of operations is dilute nitric acid, however, it is not a question of the absorption of a somewhat inconvenient product into the plant cycle, but the conversion of this product into a valuable marketable commodity.

In times of peace the greatest market for nitrogenous products is undoubtedly in agriculture; next in order of importance comes the dyestuffs industry, which absorbs nitric acid, nitrates and nitrites; finally, in a lesser degree, the industries for explosives manufacture, glass manufacture, and general chemical purposes.

Washburn, in his report to the U.S.A. Senate Committee on Agriculture in 1914, estimated the total demand for sodium nitrate in America as approximately 540,000 tons $NaNO_3$. This was absorbed as follows:—

	Per cent.
1. Mixed up with other constituents by fertilizer manufacturers	28
2. Used directly (unmixed) by farmers	17
3. Used as nitrous gases in sulphuric acid manufacture	7
4. Used for fortifying mixed acids and for nitration purposes	29
5. As an oxidizing agent in glass manufacture	6
6. As an oxidizing agent in explosives	8
7. Chemicals and miscellaneous uses	5
Total	100

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Similar figures given by White[1] for that year estimate the consumption as follows:—

	Tons $NaNO_3$.	Percent. Total.
Fertilizers	284,800	45·5
Explosives, etc.	245,400	39·2
Chemicals	95,800	15·3
Total	626,000	100·0

[1] *Met. and Chem. Eng.*, 1913.

It is clear, therefore, that there are two important types of product into which weak nitric acid may be converted, for which there is a wide market.

(*a*) Nitrates, etc., for fertilizers.

(*b*) Concentrated nitric acid for processes involving nitration.

It is proposed to consider in this chapter the production of concentrated nitric acid. The general production of synthetic nitrates is dealt with in Chapter VIII.

The Concentration of Dilute Nitric Acid

At the present time the concentration of dilute nitric acid is being carried out to an increasingly larger extent in the nitrogen industry. Concentrated nitric acid is a product necessary to very many industries at the present day, e.g. the production of dyestuffs and intermediates, nitro-compounds and explosives, the manufacture of cellulose products, various oxidation processes, etc. Dilute nitric acid, on the other hand, has very little commercial value in this form. Where supplies of concentrated sulphuric acid and a cheap source of heat are available, therefore, the concentration of dilute acid is a paying proposition and is meeting with more attention from chemical manufacturers, particularly on the Continent.

The most important methods of concentrating dilute nitric acid may conveniently be classified as follows :—

(*a*) Simple distillation and analogous processes involving heat treatment only.

(*b*) Distillation in the presence of dehydrating agents such as sulphuric acid.

(*c*) Treatment of dilute nitric acid with liquid nitrogen tetroxide.

(*d*) Electrolytic methods.

With regard to the method (*c*) above, this has already been considered in Chapter II in discussing the effect of the partial pressure of nitrogen tetroxide, and it was pointed out that such a method could not economically compete with other processes owing to the very low temperatures required for the liquefaction of nitrogen oxides from dilute concentrations of

that gas in air, and also to the amount of nitrogen trioxide remaining in the liquid at equilibrium.

The most important of the modern processes for nitric acid concentration are (*a*) and (*b*) above.

Considering the importance of the process, very little experimental work has been published concerning the method of operation. Two of the most important points to be decided are :—

1. The extent to which purely thermal concentration is economical before distillation with sulphuric acid.

2. The excess and concentration of sulphuric acid to be used.

Thermal Concentration of Nitric Acid. On long boiling of nitric acid of any concentration, the nitric acid in the distillate finally approximates to a composition of 68 per cent. HNO_3, the boiling-point of which is 121°–122° C. Variation in the pressure has very little effect on the composition of this constant boiling mixture. At 70 mm. it contains 66·7 per cent. HNO_3, at 150 mm. 67·6 per cent. HNO_3, at 1,220 mm. 68·6 per cent. HNO_3[1]. Similar figures have also been published by Creighton and Githens,[2] and by Pascal.[3] An examination of the boiling-point curve of nitric acid, obtained from the results of the above workers, will make it clear that the thermal concentration of nitric acid is not comparable with that of an acid such as sulphuric acid, whose boiling-point curve is given for comparison (Fig. 128).

The acid of minimum vapour pressure represents the maximum concentration of nitric acid it is possible to obtain by the purely thermal distillation of nitric acids containing less than 68 per cent. HNO_3. It is clear therefore that where concentrated nitrous gases are available and hence acids of 55–60 per cent. HNO_3 are obtainable from the absorption system, a purely thermal preconcentration of the nitric acid would be economically unsound. Some further light on the question is obtained by a consideration of the composition of the vapour above the surface of boiling nitric acids of various concentrations. This has been the subject of a considerable

[1] Roscoe, *Annalen*, 1860, 203.
[2] *J. Frankl. Inst.*, 1916, **179**, 161.
[3] *Ann. Chim.*, 1921, **15**, 123.

amount of work by Pascal,[1] by Carpenter and Babor,[2] and by Berl and Samtleben.[3]

The curve shown in Fig. 129 is plotted from the results of Pascal. The curve does not represent, of course, the changes in concentration of solution and vapour which occur on distilling a dilute nitric acid. It will be noticed that the per-

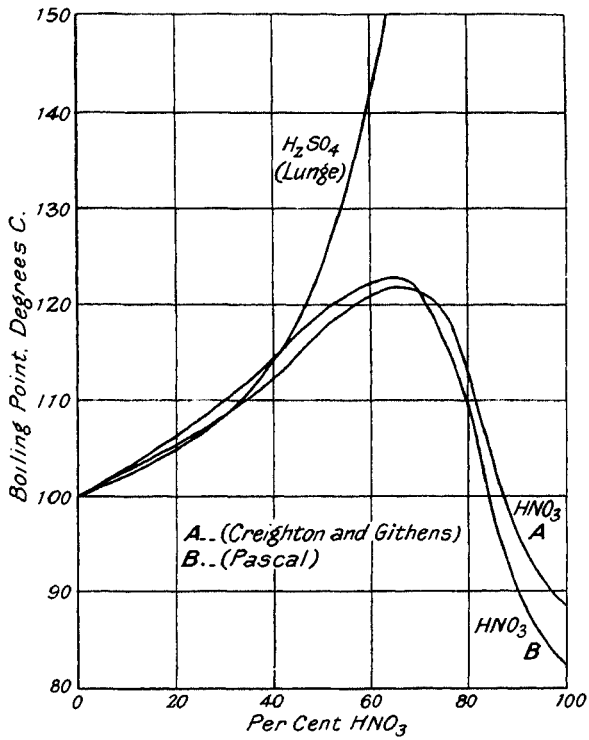

FIG. 128.—Boiling-points of Nitric Acids of different Concentrations compared with those of Sulphuric Acid.

centage of nitric acid in the vapour and liquid of a boiling nitric acid containing about 68 per cent. HNO_3 is the same. With acids of greater concentration than this the percentage of nitric acid in the vapour increases sharply to a figure of over 90 per cent.

It is evident, therefore, that by the distillation of nitric acids

[1] *l.c.* [2] *Met. and Chem. Eng.*, 1922, **27**, 121.
[3] *Zeitsch. angew. Chem.*, 1922, **35**, 201.

containing more than 68 per cent. HNO_3, the first portions of distillate obtained will contain very concentrated nitric acid, but the concentration of the residual acid will be correspondingly diminished, finally approximating to 68 per cent. HNO_3. Some experimental results of Smith[1] amply illustrate this point. A nitric acid containing 98 per cent. HNO_3 on distillation showed boiling-points rising from 88°–121° C.,

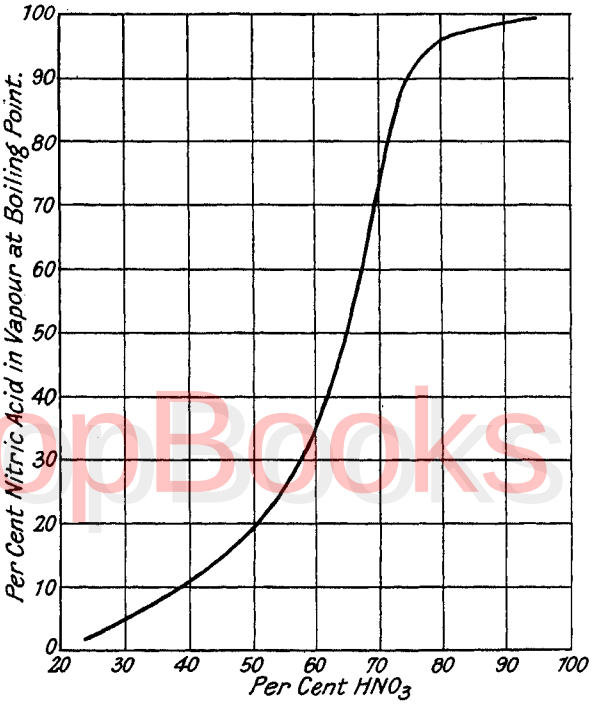

FIG. 129.—The Concentration of Nitric Acid in the Vapours above Boiling Nitric Acids of various Concentrations.

Pascal, *Ann. Chim.*, 1921, **15**, 253.

the residue left behind at the latter temperature containing only 77 per cent. HNO_3, although the first fractions obtained contained 99 per cent. HNO_3. Further distillation gave distillates containing less than 90 per cent. HNO_3, and the composition of the residue in the flask became constant at 68 per cent. HNO_3.

[1] *Pharm. Central.*, **19**, 203.

When a dilute nitric acid is distilled, however, the first fraction passing over contains almost pure water. On further heating, the concentration of nitric acid in the distillate increases fairly rapidly (the boiling-point of the solution also rising), until the concentration of nitric acid in liquid and vapour is at 68 per cent. HNO_3. This is illustrated very clearly by the experimental results of Galle [1] (Fig. 130). The dilute

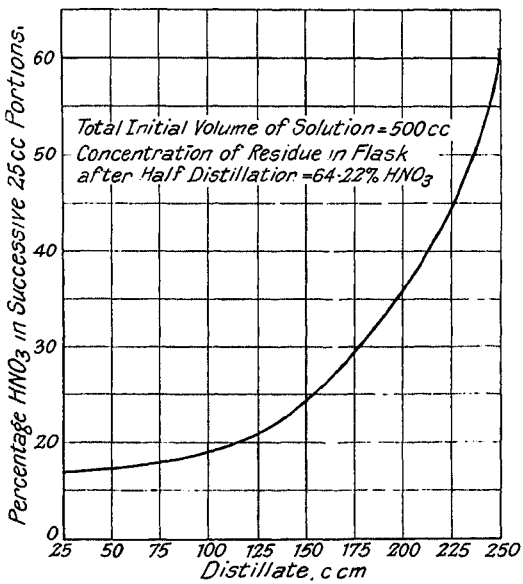

FIG. 130.—Distillation of Weak Nitric Acid.
Galle, *Zeitsch. angew. Chem.*, 1921, **34**, 168.

nitric acid used in this experiment contained 33·5 per cent. HNO_3, and it will be observed that the earlier distillates contain only 15–20 per cent. HNO_3, and not until one-half the liquid had been distilled over did the concentration of the residue in the flask rise to 64 per cent. HNO_3. The curve indicates clearly that preconcentration of nitric acid is quite possible with suitable distillation apparatus and that concentrations of nitric acid of about 65 per cent. HNO_3 are readily obtainable. The important consideration from an industrial point of view, however, is the number of fractionations neces-

[1] *Zeitsch. angew. Chem.*, 1921, **34**, 168.

sary to recover the major portion of the original nitric acid in this partially concentrated condition. In Galle's experiment no less than 50 per cent. of the liquid had to be distilled away before the residual acid reached 64 per cent. HNO_3. This 50 per cent. which had been distilled could of course be refractionated, in which case another small fraction of strong acid could be recovered, or alternatively it might be used as a feed to the absorption towers if these were not dealing with dilute gases. In the arc process, however, this would not be possible, and the problem which has still to be settled lies in the optimum concentration which should be aimed at in the preliminary thermal concentration. Some work on this point has recently been published by Carpenter and Babor,[1] who have examined the *rate* of concentration of nitric acid on distillation. Their results indicate that approximately 90 per cent. of the nitric acid (as HNO_3) in a 20 per cent. HNO_3 can be recovered as 55 per cent. HNO_3 in three fractionations, but to recover 90 per cent. of the nitric acid as 65 per cent. HNO_3 requires a very considerable number of fractionations. This result is of great importance. It has long been known that it was uneconomical to attempt to preconcentrate dilute nitric acid to higher concentrations than 50–55 per cent. HNO_3, but much work yet needs to be done to establish the optimum concentration which should be aimed at. The general conclusion to be drawn is, however, that the preconcentration of dilute nitric acids is economical. The correctness of this conclusion is emphasized when the amount of sulphuric acid required for concentration is considered. Considering the facility with which preconcentration of nitric acid can be carried out, it is surprising that the nitrogen industry has been slow to take it up, and in consequence large quantities of sulphuric acid have been wasted in concentrating very dilute nitric acids directly.

Concentration with Sulphuric Acid. Some of the earliest published investigations on the properties of mixtures of sulphuric and nitric acids are due to Saposchnikoff.[2] The representation of his results by curves is rendered somewhat difficult by the fact that the nitric acid contained dissolved

[1] *l.c.*

[2] *Zeitsch. physikal. Chem.*, 1904, **49**, 697; 1905, **51**, 609.

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nitrogen tetroxide, but the curves given (Fig. 17, p. 58) will serve to illustrate approximately the general results obtained. The sulphuric acid used in these experiments was pure monohydrate, and the nitric acid was of three different concentrations. It will be seen that in the case of a mixture of nitric acid of sp. gr. = 1·48 with monohydrate sulphuric acid, the vapour tension rises rapidly with addition of sul-

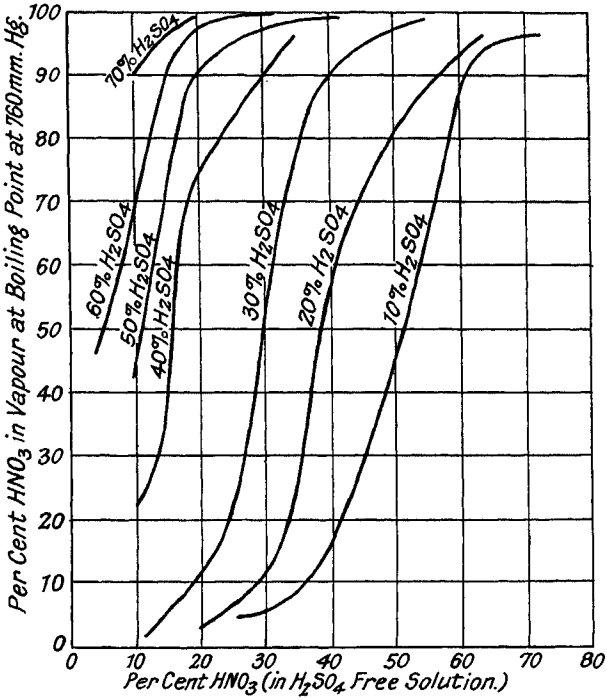

FIG. 131.—Curve showing the Percentages of Nitric Acid in the Vapour at the Boiling-point of various Mixtures of Nitric and Sulphuric Acids.

Pascal, *Ann. Chim.*, 1921, 15, 253.

phuric acid until it finally becomes equal to that of a mixture containing nitric acid of initial sp. gr. = 1·52. The maximum value occurs when the mixture contains about 35 per cent. H_2SO_4. Further addition of sulphuric acid causes a gradual fall in the vapour pressure. The analysis of the vapour shows that for mixtures containing 10–30 per cent. HNO_3, it consists of pure monohydrate nitric acid. The nitrogen content of

the vapour rises to a maximum of 24 per cent. N_2, this probably being due to the withdrawal of water from the nitric acid with the formation of nitrogen pentoxide, since the theoretical maximum for HNO_3 is 22·2 per cent. N_2. Creighton and Smith[1] have also investigated the boiling-points of mixtures of nitric and sulphuric acids at different pressures.

A considerable amount of work on the distillation and properties of mixtures of nitric and sulphuric acids has also been carried out by Pascal.[2] A very complete set of distilla-

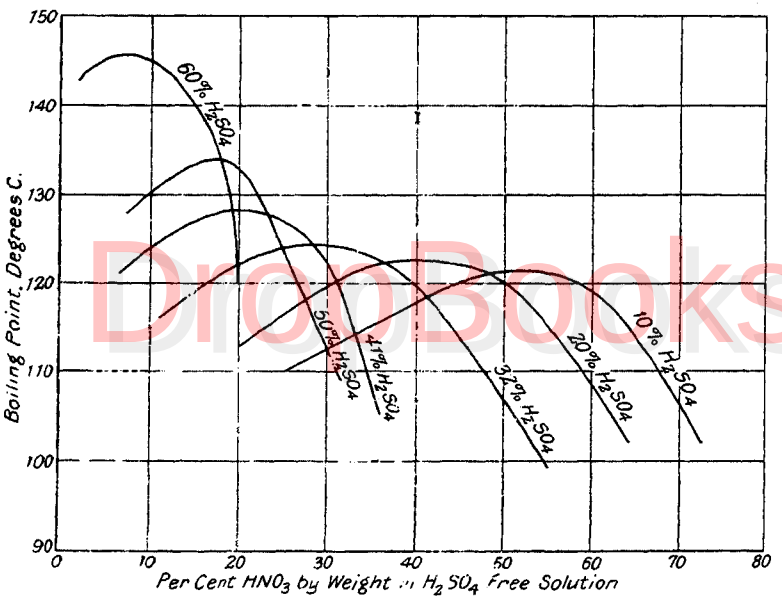

FIG. 132.—Influence of Sulphuric Acid on the Boiling-points of Aqueous Nitric Acid.

Pascal, *l.c.*

tions was carried out, using sulphuric acids varying in concentration from 10 per cent. H_2SO_4 to pure monohydrate, with which were mixed varying percentages of nitric acid. Pascal determined in each case the concentration of nitric acid in the vapour at the boiling-point. His results have been represented as curves showing the increase in concentration with that of the sulphuric acid used. The curve (Fig. 131) shows that in the presence of 70 per cent. H_2SO_4 concentrations of nitric

[1] *J. Frankl. Inst.*, 1915, 706. [2] *Ann. Chim.*, 1921, **15**, 253.

acid containing only 10 per cent. HNO_3 yield a distillate containing over 90 per cent. HNO_3. The variation in the boiling-points of the mixtures examined by Pascal is shown in Fig. 132. The observations shown are those taken at a pressure of 1 atmosphere, but Pascal made similar determinations at pressures of 300 mm., 440 mm., and 570 mm.

Perhaps the two most important points to be considered in the concentration of nitric acid by sulphuric acid are as follows :—

1. The ratio of sulphuric acid to nitric acid necessary to give efficient concentration.

2. The lowest concentration of residual sulphuric acid which is possible.

In connection with the first point, an early observation of Pelouze [1] states that five volumes of concentrated sulphuric acid are required to produce one volume of concentrated nitric acid from 30 per cent. HNO_3. Some figures are also given by Gay-Lussac.[2] An acid containing 56 per cent. HNO_3 on distillation with 2 parts of 98 per cent. H_2SO_4 gave a nitric acid containing 99 per cent. HNO_3, while a nitric acid containing initially 41 per cent. HNO_3 gave an acid containing 91 per cent. HNO_3 when heated with 4 parts of concentrated sulphuric acid. On further distillation of this acid with 2 parts of 98 per cent. H_2SO_4, a nitric acid was finally obtained containing 95 per cent. HNO_3. Galle [3] gives figures from large-scale operations for such concentrations. If nitric acid of 36 per cent. HNO_3 is concentrated directly by heating with sulphuric acid, it requires five times its weight of 98 per cent. H_2SO_4 for concentration. If the nitric acid contains initially 55–60 per cent. HNO_3, however, only 2 parts of 98 per cent. H_2SO_4 are required for 1 part of nitric acid, i.e. only 40 per cent. of the sulphuric acid required in the case of the weaker nitric acid. Some figures for experimental distillations given by Galle further illustrate this point (Table 33, p. 290).

It is thus clear that a very great economy in sulphuric acid can be effected by preconcentration of the nitric acid before concentrating with sulphuric acid, and that when the dilute nitric acid used contains about 55–60 per cent. HNO_3, only

[1] *Ann. Chim. Phys.*, **77**, 51. [2] Gmelin Kraut's *Handbuch*, 1914.
[3] *l.c.*

TABLE 33

HNO_3 / H_2SO_4.	H_2O / H_2SO_4.	B.P. Deg. Cent.	Per cent. HNO_3 in Distillate.
(Preconcentrated) Nitric Acid used = 67·10 per cent. HNO_3 (0·02 per cent. N_2O_4). Sulphuric Acid = 96·0 per cent. H_2SO_4.			
5·00	2·40	118·8	74·66
2·42	1·20	117·6	79·72
1·61	0·81	113·8	84·55
1·18	0·59	110·0	90·75
1·00	0·50	101·2	96·80
0·67	0·33	95·8	96·69
0·50	0·25	93·0	96·72
0·40	0·20	88·6	96·74
Nitric Acid = 33·48 per cent. HNO_3 (direct from towers) Sulphuric Acid = 96·0 per cent. H_2SO_4			
1·00	2·00	110·0	18·80
0·25	0·50	117·6	65·00
0·17	0·33	118·3	80·69
0·13	0·25	115·0	89·76
0·10	0·20	110·0	91·11
0·08	0·16	109·0	93·38
Nitric Acid = 46·65 per cent. HNO_3 Sulphuric Acid = 96·0 per cent. H_2SO_4			
1·72	2·0	116·0	42·95
0·87	1·0	118·3	69·36
0·50	0·5	116·3	80·07
0·25	0·33	110·6	92·44
0·20	0·25	109·0	95·54
0·18	0·20	103·3	96·45

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2 parts of strong sulphuric acid (94 per cent. H_2SO_4) per part of weak nitric acid are necessary for concentration. In the few concentration plants which are at present in operation, the sulphuric acid consumption lies around this figure, when using preconcentrated nitric acids as a starting-point.

The next point to be considered is the lowest economical concentration of sulphuric acid which may be obtained at the

end of the distillation. In this connection it should be pointed out that the work of Lunge [1] and of Lemaitre [2] has shown that nitric acid when heated with concentrated sulphuric acid tends to form nitrosyl sulphuric acid, which is exceedingly stable in concentrated sulphuric acid solution, even at the boiling-point, and it is not until the sulphuric acid is at a concentration below 75 per cent. H_2SO_4 that it is possible to remove all such nitrogen compounds completely by boiling. Some further work on the question has been published by Webb,[3] in which sulphuric and nitric acid mixtures were heated to temperatures between 100°–250° C. in order to determine the rate at which nitric acid was resolved into nitrosyl sulphuric acid under such conditions.

TABLE 34

Analysis of Original Acid.	Temperature and Time of Heating.	Analysis of Sample.		
		HNO_2 %.	HNO_3 %.	Total as HNO_3 %.
H_2SO_4 = 74·06% HNO_3 = 1·48% HNO_2 = nil	100°–110° C. for 1st hour	0·003	1·38	1·38
	110°–120° C. ,, 2nd ,,	0·003	1·30	1·30
	120°–130° C. ,, 3rd ,,	0·009	1·22	1·23
	130°–140° C. ,, 4th ,,	0·013	1·07	1·09
	140°–150° C. ,, 5th ,,	0·040	0·73	0·79
H_2SO_4 = 83·15% HNO_3 = 1·77% HNO_2 = trace	160° C. for 5 mins.	0·037	1·54	1·60
	160° C. ,, 2 hours	0·113	1·32	1·47
	180° C. ,, 3rd hour	0·307	1·06	1·46
	180° C. ,, 4th & 5th hr.	0·470	0·39	1·02
H_2SO_4 = 95·6% HNO_3 = 1·88% HNO_2 = 0·01%	160° for 30 mins.	0·016	1·67	1·88
	160° ,, 3 hours	0·032	1·45	1·88
	230° ,, 15 mins.	0·400	1·19	1·73
	230° ,, 6 hours	1·200	0·12	1·73

From these results, given in Table 34, it is clear that the

[1] *Sulphuric Acid and Alkali*, Vol. I. [2] *Mon. Sci.*, 1907, **21**, 809.
[3] *J. Soc. Chem. Ind.*, 1921, **40**, 265r.

more concentrated the sulphuric acid, the more rapidly is nitric acid decomposed into nitrosyl sulphuric acid. It is essential, therefore, to use such a quantity of sulphuric acid that the final concentration is below 75 per cent. H_2SO_4, in order to ensure complete denitration of the acid. It should be pointed out that the formation of nitrosyl sulphuric acid will be prevented to a certain extent with greater ratios of nitric to sulphuric acids, owing to the reversibility of the reaction

$$OH{\cdot}SO_2{\cdot}ONO + HNO_3 \rightleftharpoons H_2SO_4 + N_2O_4.$$

For this reason, therefore, the presence of nitrogen tetroxide in the nitric acid to be concentrated is a disadvantage, since it forms nitrosyl sulphuric acid, which is difficult to decompose. In order to denitrate the sulphuric acid completely, it is economical to use steam as a heating medium and diluent, the amount of steam being so adjusted in normal operation that the final sulphuric acid has a concentration of about 70 per cent. H_2SO_4. In this way the whole of the nitrogen compounds can be recovered from the acid without serious dilution of the distilled nitric acid obtained. This concentration of sulphuric acid, it will be remembered, is also that which obtains in good denitration practice.

The presence of hydrochloric acid in the nitric acid is also deleterious, since nitrosyl chloride is formed which must be broken down by excess of sulphuric acid, and thus increases the consumption of this latter acid.

The process of treating dilute nitric acid with sulphuric acid and a counter-current of steam is the most common type of process for concentrating dilute nitric acid.

Types of Distillation Plant. A number of different types of apparatus have been designed both for the thermal and also for the sulphuric acid concentration of dilute nitric acid. So far as the purely thermal process is concerned, the simplest type of apparatus consists of a still, externally heated, and preferably fitted with a dephlegmating column. Stills lined with acid-resisting tiles (Figs. 133, 134, 135) or constructed of iron-silicon alloy may be used, but in the former case the heating must be internal. A number of stills in stoneware have also been designed for this purpose.

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The use of stills packed with sand, quartz, or similar materials is undesirable for the initial concentration process, since overheating usually occurs, and too large a proportion of nitric acid is converted into oxides of nitrogen. The use of hot air or hot gases as a heating medium, in actual contact with the nitric acid, is also uneconomical, except in special cases, where large supplies of waste heat in this form are available. The heat capacity of such gases is relatively small, and in addition

FIG. 133.—Vessel lined with Acid-proof Tiles for use with Weak Nitric Acid.
Guthrie & Co.

nitric acid is carried away as a fine mist which is exceedingly difficult to condense, and any oxides of nitrogen which are formed are carried away in a diluted condition, and their reabsorption is somewhat difficult.

According to Galle[1] the distillation plant of Pauling has proved quite successful for the concentration of nitric acid

[1] *l.c.*

with sulphuric acid on a large scale. Successful plants have also been designed by Rossi in Italy (Fig. 137), and by the Norwegian Hydro-electric Co. at Rjuken. The apparatus of Pauling is constructed on a similar principle to the denitration tower. The tower is built of an iron-silicon alloy or

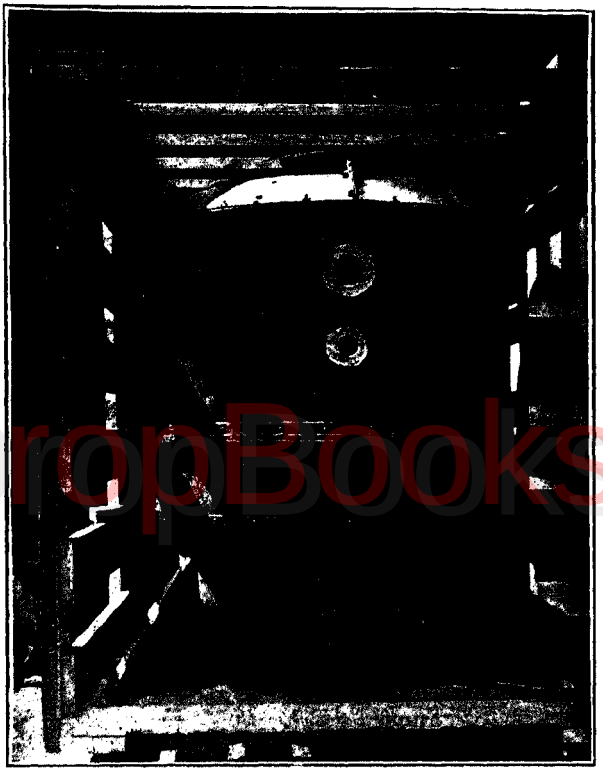

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Fig. 134.—Steel-armoured Ceratherm Heaters for Concentrated and Weak Nitric Acid.
Guthrie & Co.

alternatively of cast iron, lined with acid-resisting tiles, and filled with acid-resisting material such as quartz, or stoneware rings, etc., carried on an iron-silicon grating placed above the bottom section of the tower.

A diagrammatic representation of the Pauling tower as described by Galle is shown in Fig. 136. The dilute nitric acid

and sulphuric acid are run in at the top of the tower on to the distributor D. Passing down the tower, they meet the steam delivered in at the base of the tower by the jet S. The heat of the reaction is sufficient to drive off the nitric acid, which

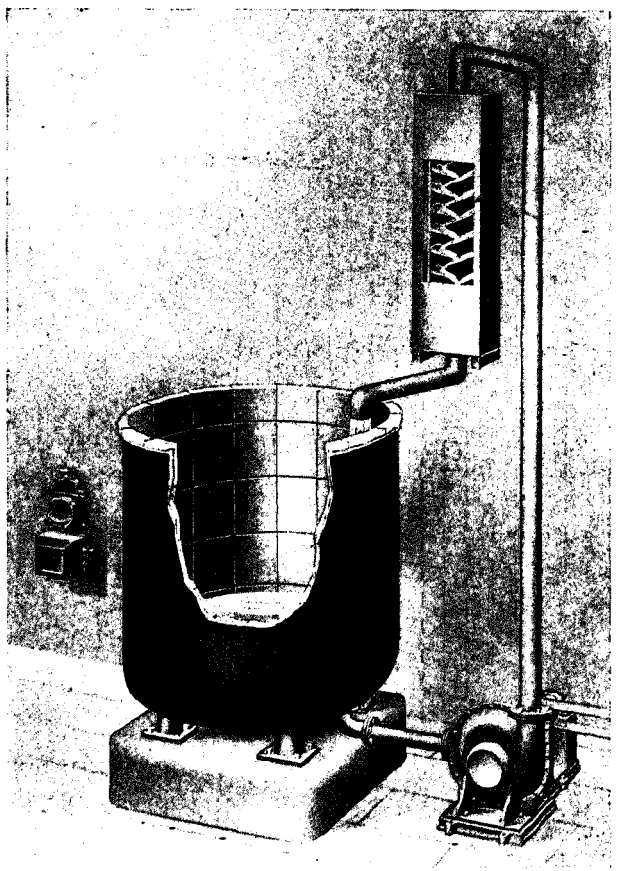

Fig. 135.—Electrical System of heating Weak Nitric Acids.
Guthrie & Co.

passes through a silica coil, or silicon-iron cooler C, completely immersed in water. Any oxides of nitrogen uncondensed are drawn off into a set of absorption towers, the weak acid from these being subsequently concentrated. The weak sulphuric acid runs out at the base of the tower at a temperature of 160°–170° C. and is passed through an iron-silicon cooler, and

then stored for reconcentration. It contains usually 0·1–0·2 per cent. nitrogen acids and 70–75 per cent. H_2SO_4. The nitric acid obtained distils off at 105°–110° C. and contains 85–90 per cent. HNO_3.

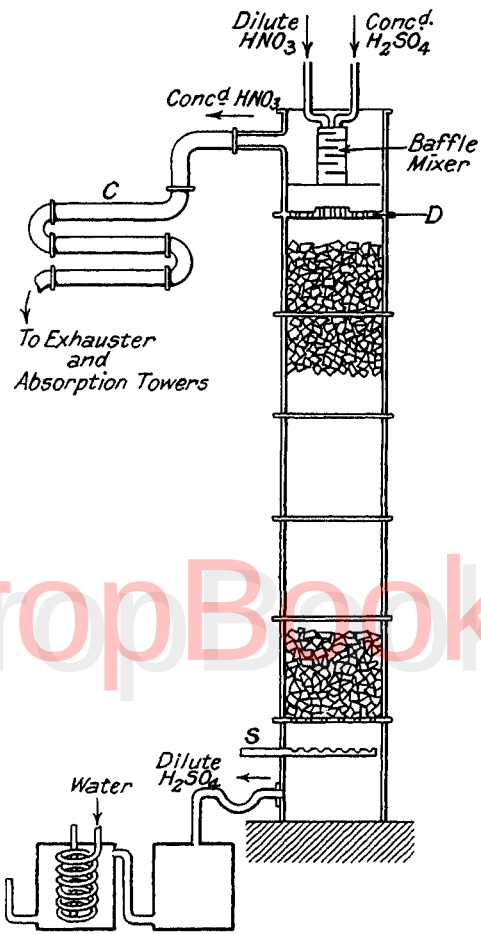

Fig. 130.—Nitric Acid Concentration Tower (Pauling).

Concentration of nitric acid has not been developed to any extent in England, and is only in its early stages in the nitrogen-fixation industry as a whole. The development and standardization of the process are proceeding rapidly, however, at the present time. A large number of patents covering the process have been put forward. These may be conveniently divided into (*a*) those covering concentration by heating; (*b*) those covering the concentration by heating with dehydrating agents; (*c*) other methods.

Concentration by Heating. Waldbauer[1] describes a concentration process, in which dilute nitric acid is run into an iron still, filled with hot granular material. The flow of acid is so regulated that only nitric acid vapour reaches the walls of the still. The packing consists of fine sand against the

[1] D.R.P. 155,066, 1902.

walls of the still, then coarse sand, and finally a core of broken flints. Collett[1] concentrates weak nitric acid by sending a blast of hot air into the still containing the acid. The still is provided with a column into which the weak acid is run and the strong nitric acid is run off from the still. A condenser is also fitted to recover weak nitric acid, and any escaping vapours are trapped by scrubbers containing quartz and lime respectively.

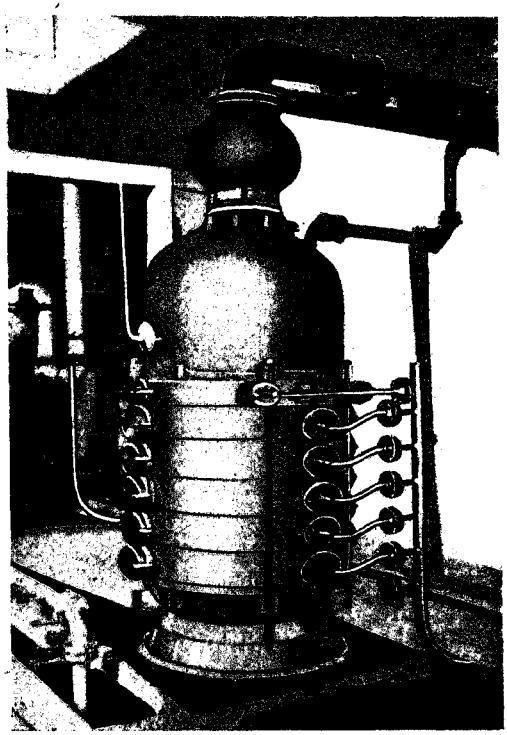

FIG. 137.—Rossi Concentration Column.
Chem. Ind., 1919 2, 11-12.

It is the normal experience, however, that the use of hot air or other gases renders it very difficult to obtain the acid of maximum boiling-point (68 per cent. HNO_3). The evaporative effect of the inert gas tends to remove excess of nitric acid vapour from the solution, leaving acids of approx. 64 per cent. HNO_3.

Another patent by the same worker[2] describes a process of concentration in which dilute nitric acid is concentrated by passage through a series of evaporators, from which the vapours are led by pipes to a dephlegmator, the acid condensed therein being returned to the evaporators. The pipes enter the deplegmator at points corresponding to the strength of the vapours, the most concentrated entering at the bottom of the dephlegmator. Dilute

[1] Fr. Pat. 357,220, 1905; U.S. Pat. 854,928, 1907.
[2] Eng. Pat. 22,746; U.S. Pat. 1,133,840; Fr. Pat. 463,859, 1913.

nitric acid containing 15–20 per cent. HNO_3 is admitted at the top of the dephlegmator to absorb nitrous vapours.

Pauling [1] recommends the distillation of dilute nitric acid from a cast-iron retort containing a layer of sand. The acid drips on to the sand and the vapours pass through a superheater and up a condensing column. A little water is admitted at the top of the column and strong acid runs off at the bottom. Rossi [2] states that if dilute nitric acid is brought into contact with heated air, so that the temperature of the air and vapours leaving the system is less than 100° C., a 75–80 per cent. yield of nitric acid containing 60 per cent. HNO_3 is obtained. Moest and Eckhardt [3] distil nitric acid which is stronger than that of the lowest vapour pressure (68 per cent. HNO_3), the vapour being sent up a fractionating column. A concentrated acid is obtained at the top and an acid containing 68 per cent. HNO_3 at the bottom. The column is maintained at approx. 100° C. and atmospheric pressure. Instead of using hot air for the concentration of nitric acid, the use of nitrous gases at a temperature of 300° C. has been suggested.[4] They are passed up a tower filled with acid-resisting material, down which is flowing dilute nitric acid preheated to a temperature of about 80° C.

PrepBooks

Concentration with Dehydrating Agents. Very many patents deal with the concentration of nitric acid to concentrations above 68 per cent. HNO_3 by the use of dehydrating agents, the commonest of which is sulphuric acid.

Frasch [5] describes an apparatus in which the still is fitted with a column, the downtake of which goes to the bottom of the still. Hot sulphuric acid runs in at the top of the column, and hot air is introduced at the bottom of the column or into the uptake from the still, to oxidize any nitrous gases present. The weak nitric acid is introduced near the top of the column, just below the entering sulphuric acid.

Valentiner [6] proposes to distil dilute nitric acid, with concentrated sulphuric acid, under reduced pressure, in order to avoid decomposition of the nitric acid during distillation. Another proposal [7] is the comparatively simple process of

[1] Eng. Pat. 27,473, 1908. [2] Fr. Pat. 455,530, 455,531, 1913.
[3] Eng. Pat. 13,842; Fr. Pat. 472,775; U.S. Pat. 1,145,162, 1914.
[4] U.S. Pat. 1,314,485, 1919.
[5] D.R.P. 82,573; Fr. Pat. 517,098, 1895.
[6] Eng. Pat. 19,192; D.R.P., 88,321, 1895. [7] U.S. Pat. 648,322, 1900.

adding dilute nitric acid to the ordinary mixture of nitre and sulphuric acid in nitric acid manufacture. This suggestion has a great deal to recommend it for simplicity and economy, the objection to it being the small capacity of the method. Since the sulphuric acid from cascade or Gaillard concentrators contains normally 94–96 per cent. H_2SO_4, and since it has been shown by Winteler [1] and by Webb [2] that sulphuric acid containing 90–92 per cent. H_2SO_4 gives the maximum yield of nitric acid with nitre, it is evident that dilute nitric acid can be added to the still to an extent sufficient to reduce the concentration of sulphuric acid from 95 per cent. to 90 per cent., which would allow of approx. 0·125 tons of 50 per cent. HNO_3 being added, per ton of nitric acid.

The use of extra sulphuric acid in the still to effect the concentration would be uneconomical, as the sulphuric acid would be converted into the relatively valueless nitre cake. Dieffenbach,[3] however, suggests the distillation of dilute nitric acid with "polysulphate," which is a mixture of sodium acid sulphate and sulphuric acid. Johnson and Baither [4] also propose to concentrate nitric acid by distillation with "polysulphate" at a temperature of 110°–120° C. The polysulphate is then heated to 250°–300° C. to remove the excess of water. Two molecules of polysulphate are required for each molecule of water in the nitric acid. Reduced pressure, and the blowing of air through the mixture, aid the process of concentration. Evers [5] describes a special type of still for the concentration consisting of a shallow pan, with two spiral flanges raised on the bottom to give a long path to the mixture of sulphuric and nitric acids. Uebel [6] suggests the distillation of dilute nitric acid with sulphuric acid in a counter-current apparatus. The nitric acid obtained is given a final dephlegmation with concentrated sulphuric acid.

Wollfenstein and Boeters[7] suggest the distillation of dilute nitric acid with water-binding nitrates such as anhydrous calcium nitrate and magnesium nitrate, which are dehydrated

[1] *Chem. Zeit.*, 1905, **29**, 820.
[2] *J. Soc. Chem. Ind.*, 1921, **40**, 222T. [3] D.R.P. 174,736, 1903.
[4] Eng. Pat. 19,986; U.S. Pat. 819,262; Fr. Pat. 358,373; D.R.P. 170,532, 1905.
[5] D.R.P. 176,329, 1904. [6] D.R.P. 210,803, 1904.
[7] Eng. Pat. 28,449; U.S. Pat. 864,217; D.R.P. 189,865; 1906.

and re-used. Uebel and Dieffenbach[1] distil dilute nitric acid with arsenic or phosphoric acids or their salts, or a mixture of the two acids. As an alternative method, the nitric acid may be distilled alone, and the vapours passed through the dehydrating agent. Sohlmann[2] concentrates the dilute nitric acid originally by a counter-current of hot gases in suitable towers. The product is then mixed with sulphuric acid and passed through externally heated pipes to drive off the nitric acid, and the sulphuric acid finally runs off into shallow pans for concentration.

Pauling[3] proposes to mix the dilute nitric acid with sulphuric acid and concentrate in towers, by a counter-current of superheated steam. The steam may carry with it suitable gases. A development of this method by Pauling[4] consists in vaporizing the nitric acid, which meets a stream of sulphuric acid at the same temperature, in a suitable concentrating tower. During the concentration the sulphuric acid is cooled.

A similar patent is described by Collett,[5] who states that in concentrating nitric acid by boiling and treating the vapours with a counter-current of sulphuric acid, regulated quantities of cooled sulphuric or nitric acids are added to keep down the temperature.

DropBooks

It has also been proposed[6] to heat a thin layer of a mixture of sulphuric and nitric acids in a shallow still, and pass a current of cold air over the surface. The floor of the still is provided with circular flanges to give a long path of travel for the mixture.

A further patent due to Collett[7] suggests the use of a series of towers at different levels. Nitric acid vapour is introduced into the bottom tower and sulphuric acid into the top tower. The vapour rises through the series of towers, and the acid leaving the bottom of the tower is cooled, part returned to the

[1] Eng. Pat. 14,831; U.S. Pat. 1,008,690; D.R.P. 238,370, 222,680; Fr. Pat. 419,166; 1909.
[2] Eng. Pat. 10,592; U.S. Pat. 1,009,197; D.R.P. 236,341; Fr. Pat. 402,709; 1909.
[3] Eng. Pat. 22,322; U.S. Pat. 1,031,864; Fr. Pat. 420,803; D.R.P. 257,809; 1910.
[4] Eng. Pat. 8,533; U.S. Pat. 993,868; Fr. Pat. 422,902; 1911.
[5] Eng. Pat. 7,597, 26,098, 1913; see also U.S. Pat. 1,154,289, 1,158,181, 1915.
[6] Eng. Pat. 20,189; U.S. Pat. 1,115,192; Fr. Pat. 462,290; 1913. See also Fr. Pat. 447,106, 450,448, 1912.
[7] U.S. Pat. 1,079,541, 1913.

top of the tower, and the rest sent on to the next tower, the process being analogous to the ordinary counter-current absorption system.

Raschig [1] describes a continuous concentration apparatus in which two stills are placed one over the other, the upper one being under vacuum. A mixture of nitric and sulphuric acids is distilled in the bottom still, which may or may not be under vacuum. The weak sulphuric acid runs out and rises to the top still under suction, is there concentrated, and then falls to the lower still. Nitric acid is added continuously to the lower still. Kaltenbach [2] describes a process in which a preliminary concentration of the nitric acid is effected by a counter-current of hot gas in a cascade of closed earthenware pans. The vapours are absorbed in a small quantity of water, mixed with sulphuric acid, and then passed down a tower packed with volvic stone, up which steam is passing.

Zeisberg [3] proposes a method of obtaining concentrated nitric acid from mixtures of nitric and sulphuric acid which result from nitration processes. The waste acid is led to the top of a cylindrical brick-lined steel tower, having a central opening filled with broken quartz. Steam is admitted at the bottom and vaporizes the nitric acid. The nitric acid vapour is led off to a condenser so arranged that uncondensed vapours can be led off to an absorption system and these are converted to dilute nitric acid, which is returned to the first tower for concentration. When applied to mixtures containing 64 per cent. H_2SO_4 and from 3–25 per cent. HNO_3, Zeisberg states that the process yields 90–97 per cent. HNO_3. In connection with this patent of Zeisberg it must be remembered that "spent" acids from nitration processes differ widely in composition. For example, those from the manufacture of T.N.T. contain usually 74–75 per cent. H_2SO_4 and 5–6 per cent. total nitrogen acids, of which only a small part is nitric acid. It would be futile in this case to attempt to obtain concentrated nitric acid by direct distillation, while denitration can only result in the ultimate production of nitric oxide and nitrogen tetroxide which must be recovered in the absorption system. In the case of the waste acid from

[1] U.S. Pat. 1,163,174, 1915. [2] *Chimie et Ind.*, 1919, **2**, 142.
[3] U.S. Pat. 1,292,948, 1919.

nitroglycerin manufacture, the nitrogen acids present in the residue consist mainly of nitric acid. Their composition is approximately H_2SO_4, 75 per cent.; HNO_3, 8·5 per cent.; H_2O, 14·0 per cent.; nitroglycerin, 2·5 per cent. In such cases a certain amount of concentrated nitric acid can be recovered by direct distillation with or without the use of steam. Unless steam is used, however, the process gives a very poor yield. In any case an appreciable loss of nitric acid occurs, owing to reduction to nitrous acid due to the presence of organic matter.

The use of dehydrating agents other than sulphuric acid has not yet been adopted to any extent for the concentration of dilute nitric acid. It is true that concentration can be carried out by the use of anhydrous calcium or magnesium nitrate, but the process is not likely to commend itself from an economical standpoint. The use of liquid nitrogen tetroxide for the direct concentration of dilute nitric acid is as yet in its experimental stages, and it is very difficult to see that such a process could offer advantages to industries in which the concentration of nitrogen oxides to be recovered is lower than 2 per cent. by volume.

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Other Methods of Concentration. Apart from the methods of concentration by direct heat and by the use of dehydrating agents, there has been a number of suggestions for the concentration of nitric acid, some of which appear to merit investigation. For example, the Tentelew Chemical Works [1] concentrate and purify commercial nitric acid, by adding it gradually to a hot solution of nickel or zinc nitrate of such concentration that the solution can be maintained at a temperature of 126°–170° C. Pure nitric acid evaporates, leaving impurities such as sulphuric acid, iron salts, etc., in solution.

Electrolytic Concentration. A recent patent for the electrolytic concentration of nitric acid is due to the General Electric Co.,[2] who propose to obtain a solution of oxides of nitrogen in nitric acid, by scrubbing oxides of nitrogen at − 40° C., and then electrolysing the solution in the presence of dilute sulphuric acid at the cathode. Hydrogen is evolved

[1] Eng. Pat. 110,637, 1916. [2] Eng. Pat. 150,836, 1920.

and anodic oxidation of nitric acid occurs, yielding concentrated acid.

Attention should also be drawn to the electrolytic methods of preparing nitrogen tetroxide mentioned in Chapter II, which may be adapted to concentrate nitrous gases and hence the nitric acid obtained from them. In this connection also the suggestion of oxidizing nitrogen tetroxide dissolved in concentrated nitric acid is of interest [1]; 17 kilos. of nitrogen tetroxide were dissolved in 80 kilos. of nitric acid (monohydrate), and the solution oxidized in the anode compartment of a cell taking 200 amps. per square metre at 7 volts. The tetroxide was completely oxidized to pentoxide by the expenditure of 11,000 amp. hours, and an acid containing 20 per cent. of dissolved nitrogen pentoxide was obtained.

Halvorsen [2] suggests that nitrosyl sulphuric acid should first be formed by the absorption of nitrous gases in concentrated sulphuric acid, and the product then dissolved in sulphuric acid, and an oxidizing agent, such as manganese dioxide, lead dioxide, or chromic oxide then added. By distillation in cast-iron retorts a concentrated nitric acid can be obtained, and the oxidizer may be recovered from the residue by electrolysis.

Cost of Concentration. Very little information is available as to the cost of concentrating dilute nitric acid. This is probably due to the fact that the large fixation plants have preferred to make, as a final product, solid nitrates and nitrites rather than free nitric acid, which has only a limited market. Furthermore the preconcentration of very dilute acid (30–40 per cent. HNO_3) to 65–68 per cent. HNO_3, before distillation with sulphuric acid, has not been adopted as yet in all cases; and the consumption of sulphuric acid is consequently excessive.

In the arc process, preconcentration can readily be carried out, utilizing the waste heat of the furnace gases, and the total cost of concentration of the 50–60 per cent. HNO_3 produced lies between £2 and £2·4 per metric ton of HNO_3 (as 100 per cent.) in the form of 93 per cent. acid. The figure in English practice is somewhat higher, being between £3–£3·5 per metric

[1] Eng. Pat. 15,432, 1911; see also D.R.P. 231,546, 1910.
[2] Fr. Pat. 363,157; U.S. Pat. 892,516; 1906.

ton of HNO_3. A recent figure covering American practice in nitric acid concentration states that the figure amounts to 15 dollars (approx. £3·5) per ton of 93–96 per cent. HNO_3. For present-day conditions, these figures are much on the low side, and certainly in this country the cost of concentration of 50 per cent. nitric acid to 93–96 per cent. HNO_3 would be at least £4·5–£5 per long ton of concentrated acid. No figures are available of the cost of the Pauling process for concentrating dilute nitric acid, though this process is reputed to give very efficient results.

The loss of nitrogen occurring during the concentration from 50 per cent. HNO_3 to 93–96 per cent. HNO_3 is usually about 3 per cent. and should not be more than 5 per cent. of the total nitrogen. The estimated production costs of concentrated nitric acid by the various fixation processes are shown in the table.

TABLE 35 [1]

Process.	Cost in £ per Metric Ton of Combined Nitrogen in the form of Concentrated Nitric Acid.
Chile Nitrate	100·48
By-product Ammonia	89·72
Arc Process:	
Power at £3·75 kwtt. year . . .	51·80
,, £2·0 ,, ,, . . .	37·08
,, £1·2 ,, ,, . . .	30·35
Cyanamide Process:	
Power at £3·75 kwtt. year . . .	54·12
,, £2·0 ,, ,, . . .	49·95
,, £1·2 ,, ,, . . .	48·05
Haber Process	44·15

The figure of £100·48 per metric ton, for the cost of pro-

[1] Report of the Nitrogen Products Committee, 1916–19. By permission of the Controller, H.M. Stationery Office.

duction of concentrated nitric acid from Chile nitrate (at £10·5 per long ton) corresponds to a figure of £22·69 per long ton of nitric acid (as 100 per cent.) in the form of concentrated acid. The average selling price of 94 per cent. HNO_3 in the pre-1914 period was approximately £23 per long ton of 94 per cent. acid, or £24·47 per long ton of HNO_3 (as 100 per cent.). The pre-1914 price of dilute nitric acid (65 per cent. HNO_3) was between £14–£15 per long ton, or between £22–£23 per long ton of nitric acid (as 100 per cent.). The figure of £30·35 per metric ton of HNO_3 as concentrated acid, given for the arc process, corresponds to £6·85 per long ton of HNO_3. There is thus a tremendous margin between the two costs, which serves to emphasize the fact that the economics of the absorption and concentration processes vary very widely with the primary cost of the fixed nitrogen.

CHAPTER VIII

PRODUCTION OF SYNTHETIC NITRATES AND NITRITES

Dilute and concentrated nitric acids are difficult materials to handle and transport in bulk, while the market for fertilizers and solid nitrates is far greater than that for fixed nitrogen in the form of nitric acid. The transport of such solid nitrates is a fairly simple matter, the greatest difficulty being due to the hygroscopic nature of some of the products. The bulk of the solid nitrates produced are those of calcium, sodium, and ammonium. The economics of the manufacture of these nitrates are not the same for all nitrogen-fixation processes, since the cost of raw material differs widely in different processes, and the availability of cheap power for evaporation, etc., is of the greatest importance. It must also be borne in mind that Chile nitrate is the important factor in fixing the market value of synthetic sodium nitrate, so far as the upper limit of price is concerned. It is generally known at the present time that the arc process is the only fixation process which can produce sodium nitrate at a price which will compete with Chile nitrate. It is calculated that a combination of the Haber synthetic ammonia process and ammonia oxidation might enable sodium nitrate to be manufactured at a price comparing favourably with the natural nitrate, but up to the present this has not been realized, mainly owing to the cost of soda ash.

It is also important to remember that it is theoretically advantageous to recover very dilute nitrous gases by the direct use of alkaline absorbents, in fact for the gases obtained in the arc process alkaline absorbents are essential, after a certain amount of scrubbing of the gases by water has taken place. The possibility of the production of solid nitrates and nitrites, therefore, by the direct absorption in alkali must be

considered as a possible alternative to the direct recovery of weak nitric acid and its subsequent conversion into nitrates. In this connection also the disadvantages attaching to the direct absorption of nitrous gases in water are fairly numerous. They may be summed up as follows :—

1. A dilute nitric acid is produced, the commercial value of which is relatively low, unless it undergoes further treatment such as concentration, etc.

2. A certain loss of nitrogen oxides or nitric acid is inevitable, unless some form of alkaline absorbent is used as a final scrubbing agent.

3. The handling and storage of dilute aqueous nitric acid in bulk requires special and expensive apparatus.

4. The size of absorption units required is very considerable, necessitating a large amount of ground space, and causing high initial construction costs. Apart from these disabilities the process has the advantages of low running costs and lack of moving parts, being practically " dead " plant, while the raw material for absorption purposes is very cheap.

So far as the direct absorption of nitrous gases by alkalies is concerned, it is well known that the process has very serious disadvantages. These will be dealt with subsequently in detail. There is at present no information available as to the relative advantages of each method of operation and they will therefore be considered separately.

Conversion of Dilute Nitric Acid into Nitrates

Generally speaking, the nitrates previously mentioned (calcium, sodium, and ammonium nitrates) are the only ones produced in the nitrogen industry by the neutralization of dilute nitric acid by the appropriate base, and calcium nitrate constitutes more than 90 per cent. of the total output.

Production of Calcium Nitrate. The cheapest available substance for neutralizing dilute nitric acid is undoubtedly limestone, and the commercial calcium nitrate produced has a considerable value as a fertilizer. This is evidenced by the fact that the Norwegian nitrogen industry produced only 1,600 metric tons of nitrate of lime in 1907, while in 1913 the output was over 73,000 metric tons. Of these quantities

215 tons were consumed (for agricultural purposes) in Norway alone in 1907 and over 5,000 tons in 1913.

The method of production of the nitrate is briefly as follows : The weak acid from the absorption towers, containing 30–40 per cent. HNO_3, is run directly from the base of the towers into large granite tanks filled with small lump limestone (Fig. 138) and allowed to stand until the resulting solution contains only 0·5 per cent. free acid. This is then neutralized with lime, and the solution evaporated in iron pans by waste heat from the furnace gases until the product is pasty and contains 13 per cent. of nitrogen. It is then run on to cylindrical granulating rolls, and the granulated product packed in casks. The "nitrate of lime" so obtained is a basic calcium nitrate containing free lime, the amount of nitrogen being about 13 per cent. While this basic nitrate is not nearly so hygroscopic as the neutral salt, it nevertheless possesses this disadvantage to a small extent. Hence the necessity for packing in wooden barrels, which materially increases the cost of the product. Since a metric ton (2,200 lb.) of nitric acid yields theoretically about 1·7 tons of nitrate of lime (13 per cent. N) it is clear that the evaporating, handling and packing side of the process forms a large proportion of the cost of manufacture. In the process of conversion of dilute nitric acid into nitrate of lime a loss of between 2–3 per cent. of the nitrogen occurs, which loss is caused by the vaporization of oxides of nitrogen during neutralization and evaporation. A small loss also occurs in handling.

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Production of Sodium Nitrate by Neutralization. The neutralization of one metric ton (2,200 lb.) of nitric acid (as 100 per cent.) in the form of dilute nitric acid yields theoretically 1·35 metric tons of sodium nitrate. The commercial product, however, contains under the most favourable circumstances 96–98 per cent. $NaNO_3$, and as the salt is hygroscopic, 1–2 per cent. of moisture is also present. The neutralization is carried out in a similar manner to that used in the production of calcium nitrate, soda ash being used as the neutralizing medium. The evaporation and crystallization of the salt is carried out in iron pans, and the resulting product divided into two commercial grades, one containing 94–95 per cent. $NaNO_3$, and the other 96–98 per cent. $NaNO_3$. The

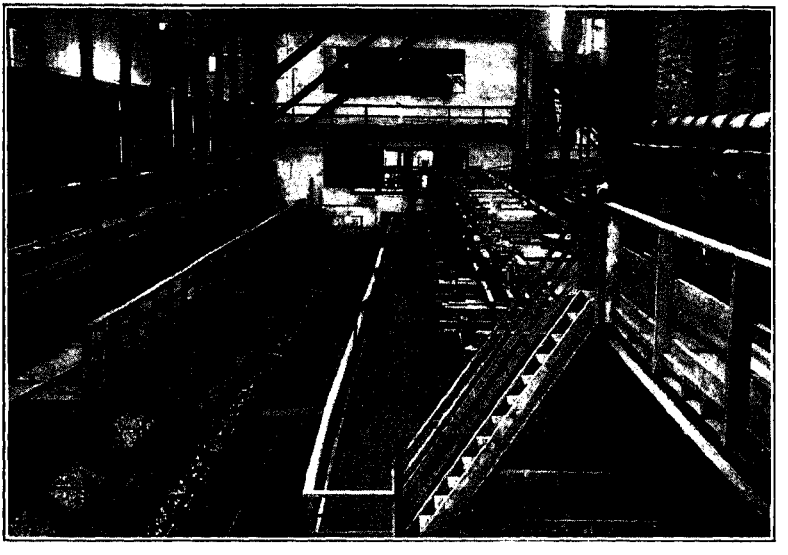

FIG. 138.—Vats for Preparation of Calcium Nitrate from Absorber Acid.

FIG. 139.—Nitrate of Lime packed for Shipment.

Norwegian Hydro-electric Company

amount of sodium nitrate produced by direct neutralization is comparatively small. The export from Norway in 1913, for example, was only 1,125 metric tons.

Production of Ammonium Nitrate. Up to the year 1914, the amount of ammonium nitrate manufactured in nitrogen-fixation processes was comparatively small. The salt was produced mainly by the neutralization of dilute nitric acid by ammonia gas, in special types of saturator. An example of such saturator in acid-resisting iron is shown in Fig. 140. The cost of evaporation in the case of ammonium nitrate is very heavy owing to the wear-and-tear on the evaporation plant and to the losses of fixed nitrogen which ensue owing to the decomposition of the salt. This has been overcome to some extent by the modification of leading gaseous ammonia into strong nitric acid of such concentration that the heat of neutralization is sufficient to evaporate off the water present, and the solid nitrate can be run off in a molten condition. The saturators can be of acid-resisting iron, carefully lagged, but cast iron lined with acid-resisting material of low conductivity has also been used with success as a construction material. The loss of nitrogen in this process is also heavy, amounting to more than 10 per cent. of the ammonia used. With improved methods of recovery, however, the process should yield much higher conversion efficiencies than this.

FIG. 140.—Nitrate of Ammonia Saturator.

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There are several processes for producing ammonium nitrate, other than the process of direct neutralization. These involve the use of sodium nitrate or calcium nitrate. For example, the ordinary ammonia-soda process may be modified by substituting sodium nitrate for sodium chloride in the series of reactions, the ammonium nitrate being separated from the liquor by evaporation after the removal of the sodium bicarbonate. The technical difficulties of the process, however, have not yet been adequately surmounted. Another method of preparation is in the interaction of Chile nitrate and ammonium sulphate. The liquor is evaporated and cooled when sodium sulphate crystallizes. Further evaporation is then carried out and a little nitric acid added. On cooling a fairly pure ammonium nitrate is obtained. The interaction of calcium nitrate and ammonium sulphate has also been suggested; but the fixing of the potential sulphuric acid as calcium sulphate is obviously uneconomical. Ammonium carbonate and calcium nitrate have also been used. Very little detailed information is at present available concerning these latter processes, but it may safely be assumed that they will not compete seriously with the direct neutralization process, so far as the direct production of ammonium nitrate is concerned.

Absorption by Alkalies

Wet Alkaline Absorption. When nitrogen tetroxide is led into milk of lime, the first reaction is the production of a mixture of nitrate and nitrite containing (in practice) a slight excess of nitrate.

$$2N_2O_4 + 2Ca(OH)_2 = Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O.$$

By continued passage of the nitrogen tetroxide, the whole of the nitrite may be decomposed with the production of a pure nitrate in the solution.

$$N_2O_4 + H_2O = HNO_3 + HNO_2,$$
$$2HNO_3 + Ca(NO_2)_2 = Ca(NO_3)_2 + 2HNO_2.$$

These reactions apply equally to the absorption of nitrous

gases by other alkaline absorbents such as sodium carbonate, magnesium carbonate, etc., and a pure nitrate may be produced in each case. If, however, the nitrous gas consists mainly of nitrogen trioxide (N_2O_3), then a pure nitrite is the resulting product. In the ordinary tower system, it will be remembered, the nitrous gases approximate more closely to the composition N_2O_3 as the gases pass through the tower system owing to the longer time of oxidation required for the increasingly dilute nitric oxide regenerated. If aqueous alkaline absorbents are used in the counter-current tower system instead of water, therefore, it will be expected that almost pure nitrate would be produced in the towers nearest the gas inlet, while at the other end of the system nitrites would be mainly produced, owing to the proportion of nitrogen trioxide present. In this connection, Pauling and the Salpetersäure Gesellschaft [1] propose to use the ordinary counter-current absorption system, with alkaline absorbents. The nitrite formed in the end towers of the series is partially removed by evaporation and crystallization, and the mother liquor then sent forward towards the gas-inlet tower of the system, when all the nitrite content is converted into almost pure nitrate, which can be recovered by evaporation.

DropBooks

A similar process [2] is one in which a 20 per cent. solution of sodium carbonate is used as the absorbent. The nitrite is separated off after the first part of the series, and the liquid then sent forward to the towers containing gases richer in nitrogen tetroxide. When a sodium carbonate solution of this concentration is used as the absorbent, the residual solution usually contains about 30 per cent. by weight of sodium nitrate, from which the salt can be obtained by concentration and crystallization in water-jacketed shakers. The use of milk of lime as an absorbent gives much weaker solutions of calcium nitrate (15–20 per cent.), owing to the difficulty of circulating a suspension of slaked lime in water, due to choking of sprays and towers by solid lime.

For the production of calcium nitrate directly, the ordinary type of absorption tower is used, packed with quartz. In some cases the towers have been built of iron and even of wood, for use with such alkaline absorbents. At Leverkusen in

[1] Eng. Pat. 9,884, 1910. [2] U.S. Pat. 991,356, 1910.

Germany, for example, iron towers were used for the absorption, by sodium carbonate solution, of nitrous gases from ammonia oxidation. In this case considerable corrosion of the towers was experienced, probably owing to the development of free acid in the towers. This may have been caused through poor liquor distribution, but was probably due to the fact that the process aimed at getting only nitrate with no nitrite, and it is well known that free acid is present in the solution in appreciable amounts before all the nitrite is decomposed. Similar towers are also used by Meister, Lucius and Brüning at Höchst.

The difficulty in the use of packed towers, when absorbents such as milk of lime are used, lies in the great tendency to choking, due to the deposition of the hydrate on the packing material. For this reason, unpacked towers, down which milk of lime is sprayed, have been suggested, and in some cases put into operation, e.g. the Badische Anilin und Soda Fabrik [1] propose to use very finely divided milk of lime in sprays for the absorption. A similar patent [2] suggests the use of glass sprays for milk of lime when used for this purpose. The use of jets, however, again brings in its train a series of troubles due to choking. With milk of lime this is quite a serious difficulty, and if the jets are made very coarse, the distribution is correspondingly poor. The disadvantages appertaining to the use of milk of lime or suspensions of basic substances in water, in the ordinary tower system, may be briefly summarized as follows :—

(*a*) If packed towers are used, choking occurs very rapidly and frequent repacking is necessary.

(*b*) The use of unpacked towers necessitates the spraying of milk of lime under pressure and consequently increased power costs, while the use of jets also gives trouble owing to choking.

(*c*) The specific gravity of milk of lime which may be sprayed is comparatively low, and consequently the solution of calcium nitrate obtained is relatively dilute, causing higher evaporation costs.

These conclusions are also supported by the fact that the

[1] Eng. Pat. 10,465, 1909.
[2] U.S. Pat. 1,029,528, 1909.

Badische Anilin und Soda Fabrik, who used the direct absorption by milk of lime in their Schönherr furnace plant, have reverted to the water-absorption system.

Many suggestions have been made for overcoming these disadvantages. The commonest type of proposal is to use various kinds of mechanical washers containing alkaline solutions or suspensions, which washers are stated to have the advantage that no obstipation takes place and the necessity for frequent re-packing is therefore avoided. Halvorsen,[1] for example, suggests the use of a suspension in water of lime, or salts of acids which are liberated by nitric acid as the absorbing medium. The use of suspensions of alkaline earth hydroxides, oxides, or carbonates in a very fine state of division has also been suggested,[2] and is very similar to the above. The direct absorption of nitrous gases by wet alkalies may be modified in a number of ways. Thus the mixture of nitrite and nitrate obtained by the direct absorption of nitrous gases in alkaline solutions may be decomposed by an equivalent amount of dilute nitric acid.[3] The nitrous gases obtained from the nitrites are mixed with sufficient air to yield only nitrogen trioxide, and the gas is then absorbed in soda, yielding pure nitrite, while evaporation of the original solution gives pure nitrate. Bosch and Wild[4] obtain commercially pure calcium nitrate by treating a solution of calcium nitrite with a mixture of nitrous gases and oxygen at a temperature between 28°–50° C. The same workers[5] also suggest that the nitrate can be conveniently manufactured by contact between oxides of nitrogen and lime and a limited supply of water, the reaction being carried out at a temperature of 280°–300° C.

Ammonium nitrate is not prepared by direct neutralization of ammoniacal liquor by nitrous gases, owing to the loss as ammonium nitrite which invariably occurs, nor can it also be prepared economically, for this reason, by modifying the ammonia oxidation process in such a way that free ammonia is allowed to escape through the catalyst chamber and combine with the nitrous gases beyond.

[1] U.S. Pat. 948,726; Fr. Pat. 380,190; 1909.
[2] Fr. Pat. 412,788, 1909.
[3] Fr. Pat. 425,997, 1911; cf. D.R.P. 220,539, 1909.
[4] U.S. Pat. 1,013,984, 1912. [5] U.S. Pat. 1,115,164, 1914.

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Production of Nitrites. It has been already pointed out that pure nitrites may be produced by the absorption of nitrous gases under suitable conditions by aqueous alkalies. Although the market for sodium nitrite is very limited, the product has a greater commercial value per unit than the nitrate, and for this reason is made to a certain extent directly from nitrous gases. For this purpose the nitric oxide initially formed is allowed to oxidize only so far as nitrogen trioxide (N_2O_3), which is absorbed directly in a solution of 20 per cent. sodium carbonate. The exact composition of gas required can be secured in various ways: in ammonia-oxidation processes, for example, by adjustment of the ratio of air and ammonia passing through the catalyst; in denitration processes, by limiting the amount of oxygen added; and in fixation processes, by limiting the time of oxidation allowed for the gases. In this way, provided that a slight excess of nitric oxide is left in the gases, a pure nitrite can be obtained by absorption in alkaline solutions. A recent suggestion to produce pure nitrites from nitrous gases, for example, proposes to divide the nitrous gas into two streams, one being kept cold and the other hot.[1] Sufficient time is allowed to the one to oxidize mainly to N_2O_4, while the other is prevented from doing so by its temperature. The two streams of gas then converge into an absorption vessel containing sodium carbonate solution, to which they are admitted in the proportions to form N_2O_3, which is quantitatively absorbed as sodium nitrite. The nitrite can be obtained readily from such solutions by evaporation.

Where milk of lime is used as the absorbent, the calcium nitrite obtained is invariably converted into nitrate, since the nitrite has very little commercial value. In this connection Hempel[2] proposes to manufacture nitrites from nitrates by heating the latter with a formate (preferably of calcium) to 300° C. *in vacuo*. In this way the nitrate is converted quantitatively into a nitrite, and the formate to a carbonate. In the case of an initial mixture of sodium nitrate and calcium formate, therefore, the resultant product would consist of sodium nitrite and calcium carbonate from which the nitrite could be extracted by water and crystallized.

[1] Fr. Pat. 441,706, 1912. [2] Fr. Pat. 388,563, 1908.

Dutt and Sen [1] point out that when nitric oxide is passed through suspensions of various dioxides in water, mixtures of nitrites and nitrates are formed. With lead dioxide (PbO_2), for example, a mixture of lead nitrate and nitrite is obtained. Barium peroxide, on the other hand, gives exclusively barium nitrite. The use of peroxides, however, in absorption practice has not been made on any considerable scale up to the present time, and it is difficult to see that the use of such substances could justify itself from an economic point of view.

Absorption in Solid Bases. The difficulties accompanying the absorption of nitrous gases in towers by circulating suspensions of basic substances, and the size of the absorption units necessary, have given considerable impetus to the examination of proposals for absorbing the gases directly in a solid absorbent. Generally speaking, the proposals cover the use of weakly basic oxides. Some of them are merely processes for the concentration of the nitrous gases by the formation of easily decomposable nitrites and nitrates (see Chapter II). There are a number of others, however, which cover processes yielding pure nitrates and nitrites. By far the most important of these processes is that of Schlöesing,[2] who proposes to use briquettes of lime at a temperature of 300°–400° C., under which circumstances only calcium nitrate is formed, the nitrite being unstable at that temperature. The process is, so far as can be ascertained, the only method of absorption by solid absorbents which has been tried on a sufficiently large scale to justify its consideration as a commercial possibility.

The presence of moisture or carbon dioxide in appreciable quantity in the gases to be absorbed is undesirable, since the former leads to a partial fusion of the absorbing material when a certain amount of nitrate has been formed, while the latter converts part of the lime into carbonate, which is comparatively useless for the absorption. The lime employed must be pure and uniform in size. It is also found that lime burnt at as high a temperature as 900° C. is unsuitable for the absorption, and the usual procedure is to slake such lime by the addition of water, so that a homogeneous product is obtained, and then

[1] *Chem. Soc. Abstr.*, 1917, ii., 85.
[2] Eng. Pat. 22,119, 1913.

to press such material into briquettes and dehydrate by passing heated neutral gases through them at a temperature of 500°–600° C.

The process has been tried on a semi-large scale at Notodden. The moisture was removed from the air supplied to the furnace by passing it through concentrated sulphuric acid, the acid being re-concentrated by the heat of the furnace gases. The amount of carbon dioxide present in air does not materially interfere with the process. Under these circumstances, the oxides of nitrogen could be completely absorbed and a nitrate of lime produced containing up to 14·5 per cent. of nitrogen, the average nitrogen content being about 14 per cent., or 1 per cent. higher than that obtained by the direct neutralization of weak nitric acid by limestone. The product always contains about 12 per cent. of free lime. Some experimental investigation of the process has been carried out in this country, but the results cannot be considered to be very satisfactory. It must also be observed that M. Ostwald [1] states that the interaction of lime and nitrogen tetroxide is always accompanied by the evolution of free nitrogen according to the equation

$$2CaO + 5NO_2 = 2Ca(NO_3)_2 + \tfrac{1}{2}N_2.$$

The Norwegian Hydro-electric Company have not apparently extended their trials of the Schlöesing process any further as yet, although it would seem to offer important economic advantages. It seems to be necessary, in any case, to investigate more completely the mechanism of the absorption of nitrous gases by solid oxides, especially the decomposition of intermediate nitrites formed during the absorption.

The oxides of zinc, copper, magnesium, and lead have also been suggested for use in the absorption of nitrous gases.[2] The nitrates and nitrites so formed, however, are not isolated, but subsequently decomposed by heating in iron retorts to 500° C., yielding oxides of nitrogen in a concentrated form. Ramsay [3] similarly suggests the oxides of aluminium, magnesium, and iron, and also the phosphates of these metals for the absorption, while Schönherr and Hessberger [4] propose to use phosphates, silicates, tungstates, etc., for the absorption.

[1] *Annalen*, 1914, **61**, 32.
[2] Fr. Pat. 388,305, 1908; cf. U.S. Pats., 1,236,662, 1917; 1,316,050, 1919.
[3] Eng. Pat. 16,067 and 16,068, 1907. [4] U.S. Pat. 1,032,782, 1908.

In view of the fact that the most profitable end product of absorption is a material which can be used as a fertilizer, the following method of recovery is of interest.[1] The gases are absorbed in an alkaline earth phosphate or in magnesium phosphate. Monacid and diacid phosphates are obtained, mixed with the nitrate and nitrite of the particular metal used. In the case of calcium phosphate, for example, the final product would consist of calcium nitrite and nitrate, together with calcium monacid and diacid phosphate. Lime or chalk is added to neutralize the acidity, and the products can then be packed and used as a manure. The view was formerly held that the presence of nitrite in fertilizers is deleterious, but it has been shown that this belief is erroneous, nitrites appearing to have no harmful influence on plant growth.

Economics of Nitrate Production. The great commercial value of solid nitrates is in their use as fertilizers. In the case of the nitrates of calcium, sodium, and ammonium, certain criteria have to be examined in order to estimate their relative value. These points are as follows :—

1. The available nitrogen content.
2. Primary cost.
3. Ease of application.
4. Influence of constituents other than nitrogen.

It must also be borne in mind that two other nitrogenous fertilizers, calcium cyanamide and ammonium sulphate, are competing products, while the natural Chile nitrate is a most potent factor in determining the market value of the synthetic product. If we assume for the moment that the available nitrogen content is the sole deciding factor, a comparison of the relative amounts of nitrogen theoretically obtainable from these fertilizers will be of interest (Table 36).

The amount of available nitrogen contained in a unit of ammonium nitrate is hence strikingly evident. In order to appreciate the true significance of the above figures, however, it is necessary to compare the costs of the fixed nitrogen appearing in the above form, and also the effectiveness of the fixed nitrogen under agricultural tests.

The pre-1914 selling price can of course be taken as a basis of comparison, but it is rather misleading, inasmuch as natural

[1] Fr. Pat. 389,864, 1907.

TABLE 36 [1]

Material.	Approximate Amount of Nitrogen from one Metric Ton (2,200 lb.) of Crude Product.
	lb.
e (96% $NaNO_3$) . . .	350
rate (13 % N)	285
nitrate (35% N) . . .	770
sulphate (20% N) . .	440
anamide (17·5% N) . .	385

ate almost dominated the market at that time, and ammonium sulphate in its turn was a reflex of the material, while the amounts of synthetic calcium nitrates were not sufficient to affect the market . The relative value of the nitrogen in these erefore will depend entirely upon their production various fixation processes. Accurate figures for are not available, and it is only possible to give an them. Valuable information in this respect is the report of the Nitrogen Products Committee, d is shown in the following table (Table 37) :—

TABLE 37 [1]

Material.	Estimated Cost of Manufacture per Metric Ton, 2,200 lb.	Cost of 1 Metric Ton of Combined Nitrogen.	
		Power at £3 per kwtt.-year.	Power at £2 per kwtt.-year.
itrate (96 % $NaNO_3$)	£	£	£
ess)	8·40	53·84	45·22
nitrate (13% N)			
ess)	6·81	52·37	43·76
um nitrate . . .	18·88	53·95	49·63
um sulphate (cyan-			
monia)	7·50	36·44	34·36
cyanamide (cyana-			
ess)	4·40	22·56	20·59
e (lowest possible			
. . . . .	6·89	44·02	—

the Nitrogen Products Committee, 1916–19. By permission er, H.M. Stationery Office.

Soda ash for neutralization of nitric acid is taken at £3 per metric ton, and the cost of ammonia for neutralization is based upon the average cost of ammonium sulphate, 1911–13. The table illustrates the approximate cost of the fixed nitrogen in each type of fertilizer, in which comparison calcium cyanamide shows up very favourably.

When the practical value of these products in agriculture is considered, however, it is again necessary to modify the relative values as shown by the costs of production. Table 38 shows the results of some practical tests carried out with the various fertilizers mentioned :—

TABLE 38 [1]

Crop.	Dressing.			
	Chile Nitrate.	Ammonium Sulphate.	Calcium Cyanamide.	Nitrate of Lime.
Barley . .	100	89	75	110
Oats . .	100	97	86	109
Potatoes . .	100	94	69	102
Mangolds . .	100	68	72	73

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The value of nitrate of lime for cereals is clearly brought out, while, in spite of its low cost, calcium cyanamide is not apparently the cheapest form of effective fixed nitrogen for these crops. This statement cannot of course be taken as being true for all types of crops, since there are so many variables which affect the results of such tests, and for some types of root crops, for example, calcium cyanamide shows up very favourably.

The general conclusion which it is intended to illustrate, however, is that the production costs of the various fertilizers do not necessarily indicate that there is not a wide market for those solid nitrates which can be produced from an absorption system. This is further supported by the fact that it is impracticable in agriculture to use only one type of nitrogen compound as a fertilizer, since each has a set of conditions for specific crops, for which it is the best and cheapest available

[1] Institute of Agriculture, Rome, 1915.

material. A general discussion on the relative value of fertilizers is outside the scope of this book, however, and it is proposed to deal briefly only with the nitrates of ammonium, calcium, and sodium. So far as ease of application is concerned, all three products are of an hygroscopic nature. Sodium nitrate is the most easily handled, but is easily washed out of the soil and, under certain conditions, is reduced to nitrite and even to nitrogen by soil bacteria. Ammonium nitrate, although containing the greatest percentage of fixed nitrogen, is also washed out of soil much too easily to be efficient. While these difficulties may ultimately be overcome, the latter material is not a serious competitor at present in the market as a fertilizer, and the amount of ammonium nitrate produced as the end product of absorption processes in times of peace is very small, and consideration can therefore be limited to sodium nitrate and nitrate of lime. Calcium nitrate has a number of specific advantages in agriculture, perhaps the most important of these being—

(*a*) It supplies lime to the soil in a soluble form, and is hence advantageous in sandy and heavy soils naturally poor in lime, or which have become deficient in lime content through various causes.

(*b*) Its hygroscopic nature is useful in dry soils, especially during drought periods.

(*c*) Nitrate of lime does not cause deflocculation in clayey soils, such as is produced by excess of sodium salts. The soil consequently does not become sticky.

The relative value of these two products, as evidenced by practical agricultural tests, indicates the superiority of calcium nitrate for certain types of growth. The development in the consumption of calcium nitrate in Scandinavia (Fig. 141) illustrates clearly the modern tendency towards the utilization of this fertilizer, and shows, furthermore, the value of the material as a product of the absorption system.

The chart is perhaps even more instructive in showing that the production of calcium nitrate must offer considerable economic advantages over that of sodium nitrate as an end product from the fixation of nitrogen by the arc process.

Apart from their uses as fertilizers, both sodium nitrate and calcium nitrate have other industrial uses: the former for

the production of concentrated nitric acid and use as an oxidizing agent, and the latter as a medium for the preparation of ammonium nitrate.

In discussing the economics of the production of synthetic nitrates, it is important to remember that the output of synthetic nitrates is small compared with the consumption of Chile nitrate and also of ammonium sulphate. In 1912, for example, the output of Chile nitrate was over 2,500,000 tons

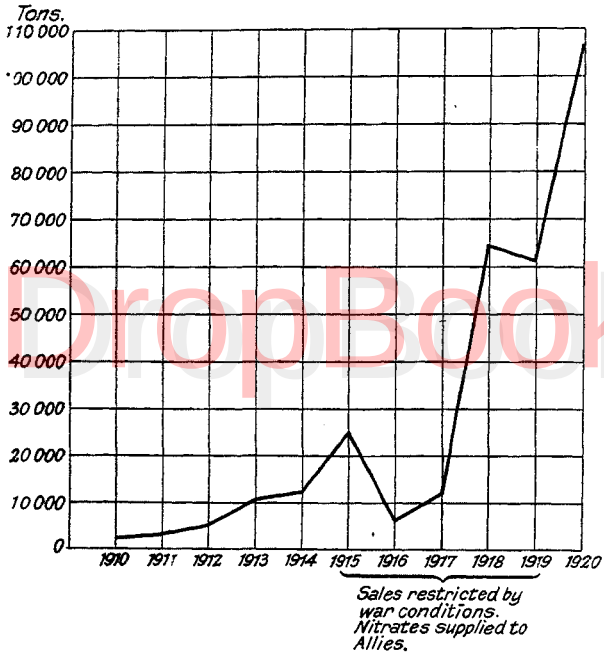

FIG. 141.—Consumption of Calcium Nitrate in Scandinavia.

and of ammonium sulphate over 1,300,000 tons, while the output of synthetic nitrate of lime reached only 75,000 tons and is less than 150,000 tons at the present time. The competition of synthetic nitrates with the natural product has not been sufficiently acute up to the present to allow of deductions being drawn as to the basic cost of production in each case. Two other important points must also be remembered—

1. The very cheap water power available to the Norwegian arc process has given the industry an unassailable position in

Scandinavia so far as home supplies of calcium nitrate are concerned, and the efficiency of the fixation process cannot be said to have been developed to the extent it would have been under greater competition.

2. The direct production of nitrates, etc., by the absorption of nitrous gases by alkaline solutions has not yet been put on a standard basis, and improvements in this direction may lead to much decreased production costs. In this connection the Schlöesing dry absorption process mentioned earlier in this chapter is stated to yield a pure nitrate containing over 14 per cent. nitrogen, and the saving in evaporation costs must therefore be considerable.

The estimated cost of production of three chief synthetic nitrates, taking the arc process as the basis of comparison, are shown in Table 39.

TABLE 39 [1]

PRE-1914 VALUES

	Nitrate of Lime, 13% N. £ per Metric Ton.	Sodium Nitrate, 95% $NaNO_3$. £ per Metric Ton.	Ammonium Nitrate. 35% N. £ per Metric Ton.
Power at £2 per kwtt.-year (normal)	5·69	7·05	17·37
Power at £3 per kwtt.-year .	6·81	8·40	18·88
Power at £3·75 per kwtt.-year (lowest possible operation cost in England)	7·65	9·41	20·01

(Soda ash taken at £3 per metric ton. Ammonia for neutralization based on average pre-1914 value of ammonium sulphate.)

The selling price of Chile nitrate (pre-1914) was approximately £10·5 per metric ton, and of ammonium nitrate £29·59 per metric ton. It is fairly clear that the arc process can make a sodium nitrate at a less cost than the amount at which the natural product is sold, but it has yet to be determined whether this would be possible if competition between the two sources

[1] Nitrogen Products Committee Report, 1916–19. By permission of the Controller, H.M. Stationery Office.

of supply became keen. It is estimated that the lowest possible extraction costs of Chile nitrate would be about £6·89 per metric ton, which is of the same order as the cost of production of the synthetic material.

In the case of processes other than the arc process, however, it is highly improbable that the production of sodium nitrate would be an economic possibility. This is illustrated by the estimate by the Nitrogen Products Committee of the cost of production of dilute nitric acid by various types of fixation processes.

TABLE 40[1]

Process.	Cost of one Metric Ton of Nitric Acid (as 100%) in the form of Dilute Acid.
	£
By-product ammonia, the cost of which is based on the pre-1914 cost of ammonium sulphate, followed by ammonia oxidation and absorption	9·36
Haber ammonia process followed by ammonia oxidation and absorption . . .	7·10
Cyanamide ammonia followed by oxidation, etc. (water power at £2 per kwtt.-year) .	8·35
Arc process. Water power at £2 per kwtt.-year	6·24

A metric ton of HNO_3 yields 1·35 metric tons of dry sodium nitrate, and would require about 0·85 metric tons of soda ash. If it is taken that commercial sodium nitrate contains only 95 per cent. $NaNO_3$ and is packed wet, the yield could be considered to be 1·42 metric tons. Taking soda ash at £3 per metric ton, the cost of sodium nitrate, using the nitric acid obtained in the processes mentioned, was estimated at £15·0, £8·0, £8·9 and £7·0 per metric ton respectively.

The cost of conversion of dilute nitric acid into sodium nitrate and calcium nitrate is considerable, and is largely affected by the cost of power. Under arc process conditions, for example, a metric ton of nitrate of lime can be produced

[1] Nitrogen Products Committee Report. 1916–19. By permission of the Controller, H.M. Stationery Office.

at a cost of £8·2 per metric ton with power at £3·75 per kwtt.-year, but the figure is reduced to £4·8 if the cheapest possible water power at £1·2 per kwtt.-year is obtainable.

The general conclusion to be drawn from the estimate of costs is that the production of nitrate of lime is economically advantageous, the product having a wide application, and in arc fixation processes is able to be produced at a cost which enables it to compete favourably with the other types of nitrogenous fertilizers on the market.

So far as the production of nitrites is concerned, sodium nitrite is a valuable end-product from an absorption system, though the market for the material is limited. The cost of production of sodium nitrite in Norway in the pre-1914 period is stated to be approximately £15 per metric ton. It is probable, however, that with by-product ammonia, followed by ammonia oxidation, using air ammonia ratios to yield N_2O_3 after the converter, the cost of manufacture of sodium nitrite would be nearly £22 per metric ton, taking soda ash at £3 per metric ton. The present market price of the material is £32 per metric ton. Owing to the market limitations previously mentioned, sodium nitrite is not made to great extent in absorption practice. In Norway the output of the material from the fixation plants was about 2,500 metric tons in 1909 and 8,200 tons in 1913.

Other Methods of Absorption

Absorption in Sulphuric Acid. The absorption of nitrous gases by sulphuric acid has been the subject of a number of patents. The reaction between nitrogen tetroxide and nitrogen trioxide and sulphuric acid is as follows :—

$$N_2O_4 + H_2SO_4 \rightleftharpoons OH{\cdot}SO_2{\cdot}ONO + HNO_3$$

$$N_2O_3 + 2H_2SO_4 \rightarrow 2SO_2\!<\!\begin{matrix}OH\\ONO\end{matrix} + H_2O.$$

Assuming that concentrated sulphuric acid is used for the absorption, the resulting solution would therefore contain a mixture of nitrosyl sulphuric acid and nitric acid. If the nitrous gas originally consisted entirely of N_2O_4, the resulting solution would contain equivalent quantities of the two substances. Small quantities of such nitrous vitriol can readily

be used in the Chamber system, by addition to the Glover tower acid.

It has been shown by Lunge [1] that nitrosyl sulphuric acid is unstable in the cold, in sulphuric acid containing approximately 64 per cent. H_2SO_4. Consequently the acid used for the absorption must be much more concentrated than this, if efficient results are to be obtained. Furthermore, the tendency to solidification of the solution, as the sulphuric acid is more concentrated, is very much increased. For sulphuric acid containing about 90 per cent. H_2SO_4 the limiting concentration is approximately 10 per cent. HNO_2 and 4·0 per cent. HNO_3. Any further passage of nitrous gases into the solution causes the separation of a nitrosyl sulphuric acid and the formation of a pasty solution which is difficult to handle.

It has been shown by Foerster and Blich [2] that N_2O_3 is more rapidly absorbed by sulphuric acid than is N_2O_4. In this connection Pauling [3] proposes to mix any residual nitrous gases which are to be absorbed in sulphuric acid, with either nitric oxide or nitrogen tetroxide, in order to secure a gas of the composition N_2O_3 and so obtain more rapid absorption. Guye and others [4] describe an absorption process by concentrated sulphuric acid in which only N_2O_4 is absorbed, and any nitric oxide is allowed to oxidize completely to N_2O_4 before being brought into contact with sulphuric acid.

The use of sulphuric acid in absorption systems is attended with a number of disadvantages:—

1. The bulk of sulphuric acid which must be circulated is relatively large, and with dilute nitrous gases the maximum nitrous acid content is 7–10 per cent. under favourable conditions, together with 3–5 per cent. HNO_3. The quantity of sulphuric acid has to be considerably increased also if solidification is to be avoided.

2. The nitrous gases are obtained mainly in the form of nitrosyl sulphuric acid, which can be utilized as such only in Chamber plants. Otherwise it must be oxidized to nitric acid by the addition of suitable oxidizing agents, or the nitrogen oxides recovered from it by denitration.

[1] *Sulphuric Acid and Alkali*, Vol. I.
[2] *Zeitsch. angew. Chem.*, 1910, 2018.
[3] Eng. Pat. 14,122, 1911. [4] Eng. Pat. 6,366, 1908.

3. The gases must be dry. Otherwise the sulphuric acid becomes continuously diluted, and loses its effectiveness for absorption. This is particularly the case when sulphuric acid is used as a final scrubbing agent for nitrous gases which have already been passed through a water absorption system.

4. The passage of inert gases through a sulphuric acid containing nitric acid results in the mechanical removal of a large proportion of the nitric acid, especially if the gas velocity is high.

5. If the sulphuric acid has to be re-concentrated after passing through the absorption cycle, the process is expensive.

These are the main objections to the use of sulphuric acid, but there are also a number of minor difficulties which arise in practice.

So far as the advantages of a sulphuric acid absorption are concerned, these are, generally speaking, far outweighed by the practical disabilities of the material.

Halvorsen [1] suggests the use of the acid as an absorbent for dilute nitrous gases in such a way that nitrosyl sulphuric acid is formed. This can then be fused in metal vessels or dissolved in sulphuric acid and transported in ordinary cast-iron or wrought-iron apparatus, thus facilitating transport; but in most chemical works the difficulties of transport of nitrogen compounds are not sufficiently acute to justify this procedure from an economical standpoint.

Nitric acid cannot be obtained in any yield by absorption of nitrogen tetroxide in sulphuric acid and subsequent distillation, owing to the reversibility of the reaction

$$SO_2\begin{matrix}<^{OH}\\ _{ONO}\end{matrix} + HNO_3 \rightleftharpoons N_2O_4 + H_2SO_4,$$

the greater proportion of the nitrogen compounds present being re-converted to the tetroxide.

If concentrated nitric acid is to be obtained, therefore, it is necessary to oxidize the nitrosyl sulphuric acid which preponderates in the solution. This cannot be done by the use of air alone, but ozonized air will effect the oxidation, although it is too expensive for commercial use. Treatment with peroxides or dioxides such as those of manganese, lead, and

[1] Norw. Pat. 15,021, 1906.

chromium will effect the oxidation. In this connection Halvorsen [1] proposes to dissolve nitrosyl sulphuric acid in concentrated sulphuric acid and add an oxidizing agent such as a chromate or the dioxides of manganese or lead. The nitric acid formed is distilled off in iron retorts, and the oxidizing agent recovered subsequently from the residue by electrolysis. Some experimental work on this type of process has also been published by Taylor Capps and Coolidge,[2] who found that concentrated nitric acid was readily obtainable in this way. They passed nitrous gases directly into hot sulphuric acid of about 90 per cent. concentration, containing chromic acid. Nitric acid was produced directly if the temperature of the absorbing solution was kept at 150° C. The nitric acid issued from the system as a mist which could be electrically precipitated and contained 95–100 per cent. HNO_3. The obvious drawbacks of the process were naturally the necessity for absorbing in a hot solution and the electrolytic recovery of chromic acid and sulphuric acid from the residual solution.

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They also attempted to produce a concentrated nitric acid by the electrolysis of solutions of nitrogen tetroxide in concentrated sulphuric acid, i.e. a solution containing nitrosyl sulphuric acid and nitric acid. Theoretically such a solution should react on electrolysis as follows :—

$$SO_2\begin{matrix}<^{OH}\\ _{ONO}\end{matrix} + 2H_2O = HNO_3 + H_2SO_4 + H_2 + 2\,\oplus.$$

On investigating the reaction, using platinum electrodes and alundum thimbles as diaphragms, they found that with low concentrations of nitrosyl sulphuric acid (10 per cent.) a current efficiency of 50 per cent. could be maintained for a short time, but the efficiency dropped to a very small value as the concentration of nitric acid in the solution increased. It must be concluded, therefore, that the use of sulphuric acid as an absorbent for the production of concentrated nitric acid is uneconomical.

In some cases, sulphuric acid is used as the absorbent, particularly with dilute nitrous gases, in order to avoid the

[1] Norwegian Hydro-electric Co. U.S. Pat. 892,516; Eng. Pat. 3,680; 1906.

[2] U.S. Bureau of Mines, 1918.

loss which inevitably occurs with water absorption systems. The nitrous vitriol so obtained is subsequently denitrated, and the concentrated nitrous gases absorbed in water or alkaline solutions. For example,[1] such nitrosyl sulphuric acid is denitrated by passing down a packed tower, where it meets the vapour of 60 per cent. nitric acid mixed with air. By condensing the vapours leaving the tower, a concentrated nitric acid can be obtained. Any nitrous gases are absorbed in water. The sulphuric acid is recovered at a final concentration of 80 per cent. H_2SO_4. A number of patents also exist for the use of sulphuric acid as an absorbent of such a concentration that nitrosyl sulphuric acid is unstable, in which case nitric acid distils off directly.

Absorption by Calcium Cyanamide. This process was originally due to Birkeland.[2] When nitrous gases, mixed with air and steam, are brought into contact with calcium cyanamide, a mixture of calcium and ammonium nitrate is obtained which may be used directly as a fertilizer. Alternatively, a solution of ammonium sulphate is added to the mixture, and calcium sulphate is precipitated and filter-pressed away. The residual solution of ammonium nitrate is crystallized, and may be converted into nitric acid by distillation with concentrated sulphuric acid or purified and used in explosives manufacture.

Calcium cyanamide is stated to absorb nitrous gases quite readily, but very little development of the process seems to have been carried out, probably on account of the cost of the material, the difficulty of securing complete decomposition, and the impurity of the salts obtained.

Absorption in Basic Nitrates. Schlarb[3] suggests the use of basic nitrates of iron, chromium, or aluminium, or compounds of these with alkalies or the alkaline earths. Lyes are obtained from such absorption from which nitric acid containing 60 per cent. HNO_3 can be distilled.

[1] U.S. Pat. 1,197,295, 1916.
[2] Eng. Pat. 25,632; D.R.P. 206,949; 1907.
[3] Fr. Pat. 422,751, 1910.

CHAPTER IX

ANALYTICAL CONTROL

It is unnecessary to emphasize the necessity for careful analytical control in absorption practice. It is too often the case that heavy losses of fixed nitrogen occur owing to insufficient routine analysis of the various products passing through the system. This is particularly the case where the load on the towers is variable; where the water supply is unreliable, and where choking or channelling through unscientific packing is liable to occur.

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The most important factors requiring analytical control in an absorption system are :—

1. The inlet gases.
2. The nitric acid produced.
3. The exit gases.

The number of compounds present in these gases, etc., differs with their origin, but the main constituents are nitric oxide (NO), nitrogen trioxide (N_2O_3), and the tetroxide (N_2O_4). In addition, nitric acid as vapour and liquid particles, nitrogen and oxygen, are almost invariably present. In the gases from a nitric acid plant, the inlet gases would contain in addition to the above gases chlorine, hydrochloric acid, and nitrosyl chloride. Ammonia-oxidation systems would give a gas containing ammonium nitrate, while in a denitration system carbon monoxide and dioxide would also be generated by the oxidation of any organic matter present, while some nitrous oxide would be produced in consequence of this reaction. In other types of gases sulphur dioxide and trioxide are also present.

The types of test required for works control are two, continuous tests and "spot" tests. It is evident that where variable working of the system is likely to take place, the most valuable method of analytical control is obtained from a large

number of intermittent tests, taken as soon as possible after each other. A continuous test alone gives merely a somewhat misleading average. It can be taken as an important general rule, therefore, that spot tests form an essential type of control test, and if continuous tests are taken, they should be interpreted in the light of evidence afforded by the individual spot tests.

As previously stated, analytical control is essential for the inlet and exit gases, and the nitric acid produced. Tests on individual towers are seldom necessary except in cases of suspected stoppage, etc.

Inlet Gases. The variables requiring to be known are :—

1. Temperature.
2. Volume percentage of nitrogen oxides.
3. The percentage of real nitric oxide.
4. The percentage of oxygen.

In some cases 2 and 4 above are more or less fixed, i.e. the nitrous gases are generated in a system where there is already considerable dilution with air, e.g. in the arc process. In other systems, such as denitration, ammonia-oxidation, etc., the amount of added oxygen should be accurately estimated and the composition of the mixture adjusted, so that its time of oxidation may be a minimum.

In systems where a steady load of nitrous gases, considerably diluted with air, is passing to the absorption towers, there is little point in carrying out regular spot tests, other than those of simple inspection, and a continuous test showing the total average nitrogen-oxide content is sufficient, provided that the temperature and time of oxidation of the gaseous mixture have been suitably adjusted. Where the supply of nitrogen oxides is irregular, and the amount of added oxygen requires to be varied within fairly wide limits, some form of spot test of both nitric oxide and oxygen is quite essential.

Exit Gases. Spot tests are absolutely necessary with the exit gases to the absorption system, in addition to continuous tests. The factors requiring examination are :—

(*a*) Total acidity as HNO_3.

(*b*) Volume percentage of oxygen.

The quantity (*a*) is made up of several factors, such as

unabsorbed nitric oxide, nitric acid vapour, and liquid particles of nitric acid in the form of acid mist. This latter usually constitutes the largest proportion of the exit losses in an ordinary absorption system.

The value of the estimation of oxygen in the exit gases lies in the convenience of control by this method, since in a closed system an exit gas containing a given percentage of oxygen (5–6 per cent.) can be shown to correspond quite sharply with an optimum mixture in the inlet gases to the system, and this method of control therefore may economize on the number of analyses to be carried out.

Absorber Acid. The weak nitric acid from the system should be weighed or measured, sampled, and the total acidity as nitric acid determined, and a separate determination made of the nitrous acid, or of the real nitric acid present.

Analytical Methods

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In general it is essential that spot tests must be rapid and approximately accurate, and preferably such as can be conveniently carried out on the plant itself. Long and involved methods which need special and complicated apparatus are usually unsuitable for works practice.

Sampling and Aspiration of Gases. In general, the ordinary sampling of gases, and the transfer of the sample to the laboratory, is not the most efficient method of operation in the routine testing of nitrous gases, etc. The time required to obtain a good sample is too long, and the possibility of error in the cycle of operations is very great. The ordinary type of gas-sampling tube which is used, however, is shown in Fig. 142. These are of glass, provided with capillary inlet and exit tubes, and should have well-fitting stopcocks. The sample is taken by opening both top and bottom cocks and allowing the gas to be sampled to sweep through the tube for 10–15 minutes. The stopcocks are then closed and the gas can then be driven over into a suitable gas-analysis apparatus at leisure.

It is possible to increase the speed at which the sample may be taken by evacuating the gas-sampling tubes by suitable means, e.g. a Geryk pump, but if evacuated vessels are to be

used at all, it is far better to use an aspirator bottle of capacity 10 litres or more. In this way errors are lessened and the sample obtained more nearly representative.

Most types of industrial gas-analysis apparatus for plant work allow of a sample of the gases being obtained rapidly and conveniently *in situ*. This is particularly the case with the Fletcher Russell bellows and the Orsat apparatus.

For continuous tests, the simplest method of operation is to aspirate a quantity of gas from a suitable part of the main into the absorption apparatus, and to collect and measure the unabsorbed gas.

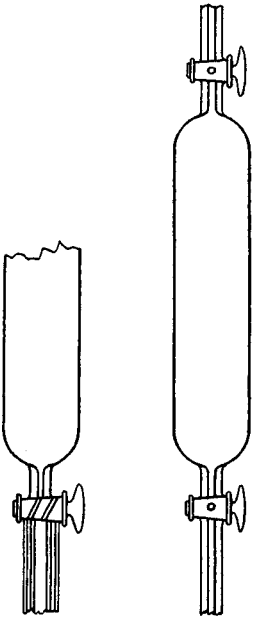

FIG. 142.—Gas-sampling Tubes.

Aspirating Tubes. For most cases where oxides of nitrogen have to be sampled, a glass tube of $\frac{1}{8}$–$\frac{1}{4}$ inch bore, inserted into the main a distance at least one-third the diameter of the flue, is most commonly used. In cases where the gases have a higher temperature than usual, e.g. 300°–400° C., a capillary tube may be used, or alternatively a silica tube of $\frac{1}{8}$–$\frac{1}{4}$ inch internal diameter, externally water-cooled. This may be done in a very simple way by enclosing it in a wider glass tube through which water circulates (Fig. 143).

Since nitrogen tetroxide attacks india-rubber very rapidly, it is necessary to use the minimum amount of rubber tubing in connecting the aspirating tube to the absorption apparatus. In fact, for continuous tests where the velocity of the gases through the apparatus is relatively low, it is advisable to use all-glass connections with fused or ground glass joints. For spot tests with the bellows this is inconvenient and also unnecessary, in view of the accuracy of the test. In this case the shortest possible rubber connection should be used, and the tubing previously dipped in molten paraffin wax and allowed to drain.

A simple type of aspirator for continuous tests is made by use of aspirating bottles placed at different levels (Fig. 144).

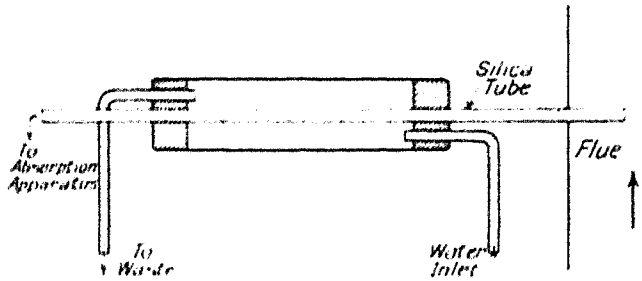

Fig. 143. Water-cooled Sampling Tube.

Since the oxides of nitrogen are very soluble in water, and in fact soluble in nearly all ordinary confining liquids, it is necessary to interpose the absorption bulbs containing aqueous

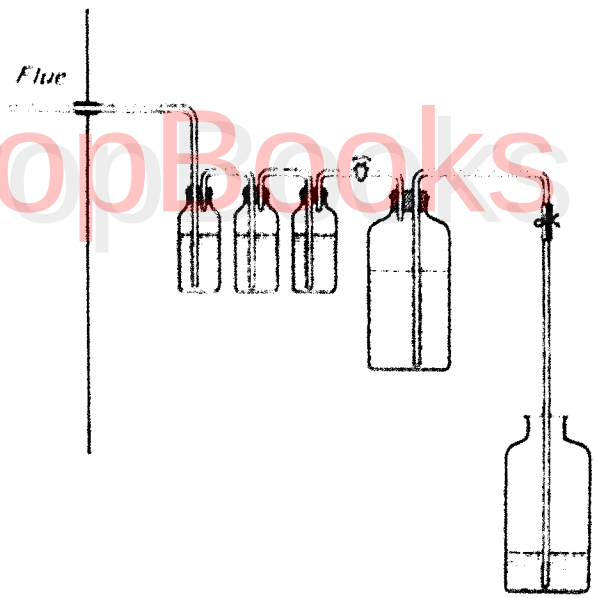

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Fig. 144. Simple Aspiration Apparatus.

alkali or similar absorbent between the aspirating tube and the aspirating bottles, in which case only the volume of unabsorbed gas is measured.

The use of aspirating bottles necessarily limits the quantity of gas which can be drawn through the apparatus, and as 10–15 litres is the normal capacity of such bottles, this represents the maximum quantity of gas which can be examined. Since the amount of oxides of nitrogen present in the exit gases from an absorption system is usually very small (3–5 grains HNO_3 per cubic foot), the total amount contained in 10–15 litres of gas would be only 1–2 grains (as HNO_3) and the determination of this amount by a titration difference method would be very inaccurate. It is necessary therefore to aspirate very much larger quantities of gas, especially if the continuous test is carried out over a 24-hour period. This can be effected with sufficient accuracy by the use of a water-jet pump, the gas after passing through the absorption bottles being measured by passing through a sensitive gas meter. A suitable type showing $\frac{1}{100}$ cubic foot is made by Alexander Wright & Co., London.

A simple type of brass injector is the Korting pump, but there are quite a number of good water pumps on the market.

In this way a large bulk of gas can be aspirated and reasonable quantities of oxides of nitrogen can be absorbed.

Sampling of Acids. The correct sampling of the weak acid obtained from an absorption system requires considerable care, as the concentration of nitric acid is varying appreciably from hour to hour, and the storage vessels attached to the plant are usually of small capacity. In fact, in small systems the acid made is often run straight into carboys. If storage vessels are available (they should be luted to prevent loss of nitric acid vapour) these should be sampled from the top and bottom layers by means of a wide glass tube which can be closed as desired at the upper end.

In the case of carboys, an aliquot portion should be taken from each by means of a dipping tube and the fractions bulked together for analysis. It must be borne in mind that nitric acid is decomposed at an appreciable rate in sunlight and errors in estimating the output of acid are often due to the indiscriminate exposure of samples of nitric acid to strong sunlight.

Analysis of Inlet and Exit Gases

Total Acidity. The measurement of total acidity is one of the simplest to carry out on the inlet and exit gases to an absorption system, and yet affords valuable evidence as to the efficiency and load of the plant. "Spot" tests of total acidity are usually determined by the Fletcher Russell bellows, or in special cases by the Orsat apparatus. Continuous tests are carried out normally by a simple type of aspiration apparatus pulling through a series of absorption bottles. The nitrous gases are usually absorbed in standard alkali and the total nitrogen subsequently determined by various methods. If the quantity of acid gases other than nitrogen oxides, such as carbon dioxide, sulphur dioxide, etc., is inappreciable, the determination of the residual alkalinity of the absorption solution, after oxidation of the nitrite present, is sufficiently accurate for most purposes. This is effected in practice by adding excess of hydrogen peroxide to the alkaline absorbent after absorption, and warming to 60° C. The alkaline solution used for absorption must be dilute, as it has been shown that the rate of absorption of nitrous gases is retarded by increase in the concentration of caustic soda in the solution beyond a certain optimum value, which corresponds approximately to a normal solution. An excess of 20 vol. hydrogen peroxide may also be added to the solution used as an absorbent, either in the bellows or in absorption bottles. The velocity of oxidation of a nitrite by hydrogen peroxide in alkaline solution is relatively slow. Moser[1] shows that 6–12 minutes are necessary. Consequently, warming the solution to 60° C. for some minutes after absorption of the nitrous gases, is advisable. An excess of $\bar{N}\cdot H_2SO_4$ should then be added and the solution boiled and the excess of sulphuric acid titrated in the usual way.

In addition to the simple method of estimating the total acidity by titration, there are a number of alternative methods by which the total nitrogen may be estimated in the alkaline solution, e.g.:—

1. By the Lunge nitrometer.

[1] *Zeitsch. anal. Chem.*, 1911, **40**, 1.

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2. By various reduction methods, of which the best are :—
   (*a*) By Devarda's alloy.
   (*b*) By ferrous sulphate (Schlöesing).
   (*c*) By titanium sulphate (Knecht).
   (*d*) By aluminium or aluminium amalgam (Pozzi Escott).

These methods will be considered subsequently.

Bellows Test. The Fletcher Russell bellows, which is so widely used in chemical industry, needs special mention. The bellows consist of an india-rubber concertina fastened to ebony plates at each end. Leather straps are fixed to these plates under which the hands pass. On one of the plates is a small ebony boss, containing an outlet to the air independent of a central outlet which is contained in a central tube in the boss,

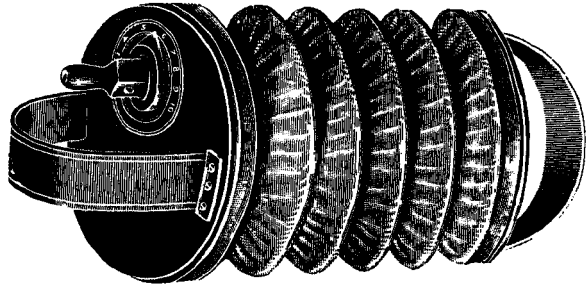

FIG. 145.—Fletcher Russell Bellows.
Baird & Tatlock, Ltd.

and which is the main path of travel of gases drawn in to the bellows. The first outlet serves as a path through which gases may be expelled which have been washed with absorbent in the bellows. In this way, the return of the washed gas through the sampling tube is avoided.

The ordinary type of bellows has a capacity of approximately $\frac{1}{10}$ cubic foot, but each one should be calibrated before use and re-calibrated every month while in continuous use.

To calibrate the bellows, a simple method is to compress them, and partially fill with water by suction and thoroughly rinse. (If the rubber is new the bellows should be given a preliminary rinsing with caustic soda solution, followed by dilute sulphuric acid and finally with water.) The inlet valve

of the bellows should then be placed under water and the bellows drawn out to their full capacity. The outlet and inlet valves should then be closed by the fingers, the bellows turned upright, and shaken to remove air bubbles. A little water should be expelled by compression and then the inlet valve again placed under water and the bellows filled. The water is then driven out into a graduated cylinder and measured. An alternative method consists in drawing out the bellows to their fullest extent, and expelling the air into an inverted measuring vessel filled with water and measuring the volume of air(s) (corrected for temperature and pressure), or the volume of water displaced.

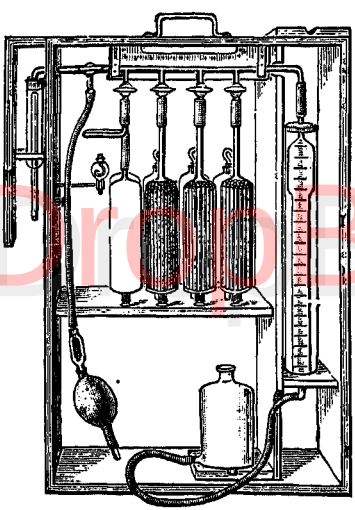

FIG. 146.—Orsat's Gas-analysis Apparatus.

Messrs. Townson & Mercer.

When estimating the total acidity of nitrous gases, 400 c.c. of N caustic soda, to which 50 c.c. of 20 vol. hydrogen peroxide have been added, are drawn into the bellows. The apparatus is then exhausted of air by compression, and a small quantity of the gas to be tested is rapidly drawn through the aspirating tube and expelled into the air. In this way the bellows are cleared of air. The bellows are then pulled out to their fullest extent, both inlet and outlet closed by the fingers, and the apparatus shaken vigorously for 2 minutes. The operation is repeated from 2 to 5 times according to the concentration of the gases being tested, and the bellows then washed out, and the absorbing solution treated in the manner desired.

Orsat Gas-analysis Apparatus. Apart from the Fletcher Russell bellows, the Orsat apparatus is the most commonly used for " spot " tests on acid gases. The apparatus is shown

in Fig. 146. The two-way tap on the left allows a sample of gas to be drawn into the measuring bulb, and expelled to the air, after the finish of the absorption. The gas is drawn into the measuring tube by lowering the bottle at the base of the apparatus. After being measured, the gas is driven into the appropriate absorption bulb, by raising the bottle and opening the tap connecting the absorption bulb with the common supply tube. The gas is passed in and out of the bulb several times, by raising or lowering the pressure bottle, and is finally drawn back into the measuring tube and the contraction measured. The confining liquid used is usually water containing about 10 per cent. of glycerine. For use with nitrous gases, the nature of the confining liquid is an obvious limitation to the general use of the apparatus.

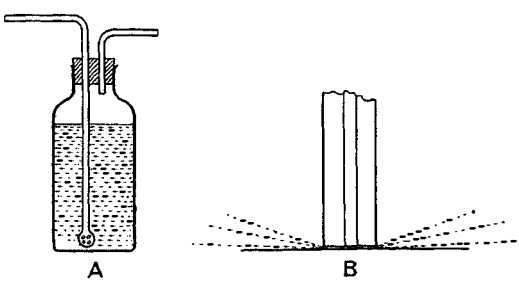

Fig. 147.

Continuous Test of Total Acidity. The apparatus used for a continuous test of total acidity over a 24-hour period is practically that shown in the diagram on page 334, except that instead of using two aspirating bottles, the unabsorbed gas is drawn through a sensitive gas meter by means of a water-jet pump. The absorption bottles should be preferably long and narrow and of the type which cause good distribution of the gas. A common type of bottle is shown in Fig. 147 (A), in which the inlet tube is expanded to a bulb pierced with a number of holes, which gives fairly good distribution.

A device which gives very good distribution of the gas, in the shape of fine bubbles, consists in grinding the end of a capillary tube, so that it rests nearly flat on the bottom of the absorption bottle. The gas drawn through is shot out from

and if the gases are bubbled through the absorbing solutions too rapidly, nitric acid vapour may be carried away in the gases, even in the presence of aqueous caustic alkalies.

It is advisable, in a continuous test, to interpose a bubbling tube containing acidified permanganate, between the last absorption bottle and the gas meter, in order to trap any nitric oxide which may have escaped absorption.

The caustic soda used for absorption should be an approximately normal solution and the quantity used will naturally vary with the period of the test and the concentration of the nitrous gases in the gas under examination. An excess of hydrogen peroxide, over that required to oxidize all the nitrite formed, should be added. If the sensitive gas meter and water-jet pump are available, 40–60 litres of gas should be drawn through over a 24-hour period. If aspirating bottles only are available, they should be changed two or three times over a 24-hour period, using the same alkaline-absorbing solutions.

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It should be noted that the volume of water run out, or the volume shown by the gas meter, is not the true volume of the gases, since the oxides of nitrogen have been removed before measurement. The same remark also applies, but to a much smaller extent, to the bellows test. It is true that the total acidity as nitric acid can be calculated to correspond to a given volume of nitric oxide or nitrogen tetroxide, but a number of complications are introduced by the temperature of the gases and the degree of dissociation of the N_2O_4. There are two methods of expression of the results in common use :—

(*a*) To express the result as so many grains of HNO_3 per cubic foot of unabsorbed gas.

(*b*) To express the number of grains of HNO_3 in a given weight of total gas.

The second method of representation gives the most accurate idea of the loss of nitrogen taking place, but the former method is usually preferred in works practice, since by measuring the total volume of gas evolved, and using the figure expressed in this way to show nitric acid loss, for example, the figure for the total loss has always a plus error which constitutes a factor of safety.

The method previously mentioned, viz. the calculation of

the total nitric acid obtained as nitric oxide or nitrogen tetroxide, is deceptive—particularly in the exit gases from the system, where a considerable proportion of the loss is due to actual liquid particles of nitric acid in the form of mist, which occupies relatively little volume.

to absorption practice where nitrogen tetroxide and nitric acid vapour are almost invariably present. The same worker also states that alkaline sodium sulphide will absorb nitric oxide, but the reaction is too slow for analytical purposes.

The use of such absorbents in absorption practice for the estimation of nitric oxide is therefore inadmissible.

Oxidation to Nitric Acid. This type of method is the most useful for works practice, although the general methods in use are not completely satisfactory. The common oxidizing agents available are hydrogen peroxide, acidified potassium permanganate, and potassium bichromate.

The use of hydrogen peroxide in this connection was first proposed by Schönbein,[1] and has since been tested by a number of investigators, including Lunge [2] and Moser.[3] This latter worker recommends the use of a special absorption bulb designed by himself, and states that six to twelve minutes are required for the complete absorption. The method has also been tried by the author, and it was commonly observed that appreciable quantities of nitrous acid could be detected in the solution when neutral hydrogen peroxide was used as the absorbent. The results obtained are somewhat inaccurate unless the time required for the reaction is borne in mind.

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Knorre [4] uses a saturated solution of potassium bichromate containing one-fifth its volume of concentrated sulphuric acid, the absorbent being stable, and does not evolve oxygen on agitation with inert gases as is possible with acidified permanganate solution.

Moser [5] leads gases containing nitric oxide directly into acidified standard potassium permanganate, and determines the amount of permanganate used up by the ordinary methods. The methods proposed by Knorre and by Moser both give accurate results with gases consisting of almost pure nitric oxide. Both the absorbents can be used in the ordinary type of gas volumetric apparatus. It is preferable, however, to determine the amount of the oxidizing agent used up by the ordinary methods of volumetric analysis, as, if the absorbent is shaken up with the nitric oxide in a nitrometer, for example,

[1] *J. pr. Chem.*, 1860, 265. [2] *Zeitsch. angew. Chem.*, 1890, **3**, 568.
[3] *Zeitsch. anal. Chem.*, 1911, **50**, 401.
[4] *Chem. Ind.*, 1902, 534. [5] *l.c.*

and the unabsorbed gas is measured, the vapour pressure of the nitric acid formed is likely to cause appreciable error.

Oxidation of Nitric Oxide to Higher Oxides of Nitrogen. As is well known, the addition of oxygen or air to nitric oxide causes the immediate formation of nitrogen trioxide, which is probably formed by the combination of the NO_2 initially formed with some unoxidized NO (see Chap. I). If the addition of air or oxygen is made in the presence of a substance which will absorb N_2O_3, the whole of the original nitrogen tetroxide can be absorbed as nitrogen trioxide, and the volume of oxygen used affords an indication of the amount of nitric oxide originally present.

Klinger [1] passes dry air into the gas containing nitric oxide, standing over sticks of caustic potash, which must be perfectly dry. The whole of the gas is absorbed as N_2O_3.

$$4KOH + 4NO + O_2 = 4KNO_2 + 2H_2O.$$

Hence four-fifths of the contraction observed on adding a measured volume of air or oxygen is nitric oxide. If the caustic potash is moist, some potassium nitrate is formed and nitric oxide is regenerated, and the method becomes inaccurate. This is particularly the case when aqueous potash or soda is used.

Koehler and Marqueyrol [2] recommend the use of monoethyl aniline as the absorbent for N_2O_3, which is rapidly and quantitatively absorbed by this reagent. The absorbent has an advantage also over caustic potash in that it does not absorb N_2O, N_2, CO_2 or CO in sufficient quantity to affect the accuracy of the determination.

Reduction Methods. Nitric oxide is reduced by hydrogen in the presence of heated platinum. Knorre and Arendt [3] pass a mixture of nitric oxide and hydrogen through a capillary tube containing platinum black heated to redness. If the speed of the gas and the temperature are correctly adjusted, the nitric oxide is quantitatively reduced to nitrogen. The method is very liable to error, however, owing to the possibility of formation of the lower oxide of nitrogen and also ammonia, and the method is unsuitable for works practice.

[1] *Ber.*, 1912, **45**, 3231.
[2] *Bull. Soc. Chim.*, 1913, **13**, 69. [3] *Ber.*, 1899, **32**, 2136.

Of all the methods previously reviewed, the best are those due to Knorre and to Hoser, and either of these may be used where considerable accuracy is desirable.

Estimation of Nitric Oxide in the Presence of Nitrogen

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(*q.v.*). If the nitric oxide is in excess of the amount required to form N_2O_3, this method is of course inaccurate.

A method proposed by Geake and Squire[1] uses acidified permanganate contained in an evacuated bottle as the absorbent. The general method of operation consists in putting a small quantity of dilute permanganate in a bottle of known capacity and evacuating the latter by suitable means, e.g. a Geryk pump. By means of a curved tube fitted with a tap, and leading into the bottle, a sample of gas is allowed to rush into the bottle, the tap being closed before atmospheric pressure is reached. The pressure is then determined by connecting to a suitable measuring apparatus. An Orsat is convenient to use for this purpose, and then the percentages of oxygen and carbon dioxide in the gas are measured. The nitric oxide is determined by titration of the permanganate by ferrous ammonium sulphate, followed by a determination of the nitric acid present by the Bowman-Scott method, from which the amount of the tetroxide can also be determined. The error caused by the entrance of nitric acid vapour is allowed for by correcting for the vapour pressure of the nitric acid in the absorption tower through which the gases have passed. This, however, is somewhat inaccurate, since a very appreciable amount of nitric acid is carried along in the vapour as liquid particles and not as vapour.

The estimation by permanganate as modified by Geake and Squire is applicable, whether or not the amount of nitric oxide present in the gases is greater than that required to form N_2O_3. For ordinary practice it is unnecessary to use an evacuated bottle. The permanganate should be contained in ordinary gas-absorption bottles and the volume of residual gas measured. From the quantity of nitric oxide and nitrogen tetroxide indicated, the volumes can be calculated to give sufficient accuracy for the purpose required. In cases where the nitric oxide is in excess of the percentage required for N_2O_3, the absorption may also be carried out in absorption bottles containing concentrated sulphuric acid, and the gases then passed through a final absorption tube containing acidified permanganate. The presence of nitric acid vapour in the gases under examination presents a difficulty which has not been satis-

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 367T.

factorily solved up to the present. The author has used a method in which the gases to be examined were passed through glass wool to remove liquid nitric acid, and then through loosely packed dry limestone or anhydrous calcium nitrate, before passing to the absorbing bottles. In this way nitric acid vapour and mist is removable without appreciable loss of nitrogen oxides.

Generally speaking, methods depending on volume changes are inapplicable to the analysis of nitrous gases in an absorption system, since nitric oxide, nitrogen tetroxide, and oxygen and nitrogen are almost invariably present together.

Nitrous Oxide, N_2O.

In some denitration processes nitrous oxide is present with nitric oxide and nitrogen tetroxide, being produced by the oxidation of organic matter by nitric acid. It is present usually to an extent of less than 0·5 per cent. by volume, and does not interfere with the absorption reactions. It may be estimated with sufficient accuracy by passing the gaseous mixture over moist stick potash, which removes oxides of nitrogen and carbon dioxide, and estimating the nitrous oxide in the residual gas by solution in water in a suitable gas burette.

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Estimation of Oxides of Nitrogen mixed with Nitrosyl Chloride and Hydrochloric Acid. This mixture of gases is commonly obtained at the exit to a set of absorption towers attached to a nitric acid plant, the chlorine compounds being derived from the sodium chloride present in the nitre. The method of analysis is similar to those previously described. The gas is absorbed by aqueous alkali containing hydrogen peroxide, and the total nitrogen present estimated by the Devarda reduction method, and the total chloride by the addition of excess of silver nitrate solution and nitric acid, and titration of the excess of thiocyanate.

Oxygen.

The estimation of the excess of free oxygen in inlet and exit gases is usually carried out after the nitrous gases have been taken out by one or other of the methods previously mentioned. It must again be pointed out that there is some uncertainty as to the exact volume percentage of oxygen,

owing to lack of knowledge of the state of dissociation of the nitrogen tetroxide. In the exit gases, where the amount of tetroxide is small, this error is inappreciable.

Estimation of Nitric and Nitrous Acids and their Salts

The general methods of estimation may be roughly classified as follows :—

1. Simple titration methods.
   - (*a*) By alkali.
   - (*b*) By ferrous sulphate.
   - (*c*) Bowman and Scott.
   - (*d*) Pelouze.
2. The nitrometer method and other methods depending on the measurement of a volume of gas produced by reduction of the nitrate or nitrite, e.g. Schlöesing method and the modified Schlöesing-Wagner method.
3. Determination as ammonia.
   - (*a*) By reduction in alkaline solution.
     - (1) With aluminium and aluminium amalgam (Pozzi Escott).
     - (2) With Devarda's alloy.
     - (3) By zinc dust and iron powder.
     - (4) By titanium sulphate (Knecht).
   - (*b*) Reduction in acid solution.
     - (1) By reduced iron.
     - (2) By reduced iron and zinc.
4. Gravimetric methods. "Nitron," etc.
5. Phenol sulphonic acid method.

It is proposed to deal briefly with the methods of analysis most useful to the industry under consideration first, and not to follow the classification outlined as to the order of treatments of the various methods.

The simplest method of estimating the nitric acid in a sample of that acid containing only nitrous acid as impurity is by titration with standard alkali. As is well known, litmus, methyl orange, and phenolphthalein are all decolorized by nitrous acid, but this difficulty can be overcome by not adding the indicator until the neutral point is nearly reached, and then titrating rapidly. Alternatively the indicator methyl red may be used. This is only very slowly acted upon by

nitrous acid.[1] A comparison between the results obtained by direct titration of a nitric acid containing nitrous acid with those obtained by reduction in alkaline solution by the Devarda method are shown in the table.[2]

TABLE 41

Expt. Number.	Percent. Total Nitrogen as NO_2 by direct Titration, using Methyl Red as Indicator.	Percent. Total Nitrogen by Devarda.
1	0·49	0·49
2	0·42	0·42
3	0·32	0·36
4	2·09	2·04
5	2·33	2·32

The agreement is very close. For works practice the simple titration with caustic soda or potash solution is usually adopted, therefore. A comparison of the difference in titration obtained by using methyl orange instead of methyl red as indicator is shown in the following table :—

TABLE 42

Expt. Number.	Titration using Methyl Orange. c.c. N.NaOH required.	Titration using Methyl Red. c.c N.NaOH required.
1	6·0	5·8
2	9·6	9·6
3	10·2	9·9
4	13·3	13·3
5	15·9	15·6
6	116·4	116·4

In practice, the device of adding the indicator near the neutral point makes it possible to use almost any of the common indicators if the amount of nitrous acid present is not too high.

Apart from the simple titration method, there are a number

[1] Koehler, Marqueyrol and Jovinet, *Ann. Chim. Anal.*, 1913, **18**, 45.
[2] F. P. Dunn, unpublished communication.

of general methods of estimating nitric acid and nitrates which are of importance in the working of absorption plants.

Nitrometer Method.

The nitrometer is very widely used in chemical industry for the estimation of nitric acids and nitrates. The apparatus and method of manipulation are described in most textbooks

From the magnitude of these quantities it is clear, therefore, that a correction should be applied for the solubility of nitric oxide. It is also advisable to use the bulb type of nitrometer where the volume of gas released is 100 c.c. or more. Finally, the question of the accuracy of Tower's correction for the solubility should be ascertained. In an investigation carried out by Dr. M. Taylor and the author,[1] it was shown that Tower's

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Temperature Fluctuation. It has been repeatedly emphasized by Lunge, and, amongst other investigators of the nitrometer method, by Newfield and Marsh[1] and by Marqueyrol and Florentin,[2] that the temperature of the apparatus must be allowed to assume a constant value before taking the

monoxide and dioxide. The nitrometer method is not available for the estimation of nitrogen in celluloid and other substances containing carbon ring compounds. E. G. Beckett [1] states that the ordinary nitrometer gives trustworthy results

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alternative method, the normal HNO_3 may be weighed out by means of the Lunge-Rey pipette.

The ferrous sulphate solution is then added from a burette, with constant agitation, until the appearance of a pinkish brown colour. The recognition of the correct shade of colour requires a little practice. From the consumption of ferrous sulphate solution, 0·2 c.c. is deducted, this being the excess required to give a pronounced coloration

1. Air dissolved in the hydrochloric acid.

2. Air and carbon dioxide from the water employed, unless distilled and recently boiled water is used. In the modified method devised for use with explosives, the nitric oxide is collected over caustic potash solution by the aid of a current of carbon dioxide, and in this form is subject to the following errors :—

1. Gaseous impurities from the CO_2.

2. Air from the hydrochloric acid.

3. Loss of nitric oxide due to decomposition and absorption by the caustic potash.

These errors compensate each other if the estimation does not occupy more than 20–25 minutes. Pellet [1] prefers Schlöesing's method for the estimation of nitric nitrogen in gun-cotton, nitroglycerin, and similar products. He also discusses the sources of error in the method. Seydel and Wickers [2] also state that the method gives accurate results even in the presence of organic matter (except urea).

Ruff and Garsten [3] state that the presence of arsenites or sulphides in a solution of nitrates or nitrites gives rise to errors in the Schlöesing method. Arsenites cause a loss of nitric oxide owing to the formation of nitrous acid, which passes over into the nitrometer. If the solution is neutral, nitrates are not reduced by arsenites. Sulphides, however, prevent the use of this method of estimation, the nitrous acid

workers determine the amount of unchanged ferrous salt in the solution by titration with permanganate solution.

About 1·5 gram of pure iron wire is placed in a flask with a long neck, and the air displaced by a current of pure carbon dioxide (2–3 minutes); 30 c.c. of pure concentrated hydro-

of the nitrate containing approximately 0·5 gram HNO_3 is added to a Kjeldahl distilling flask, and 50 c.c. of strong caustic soda solution (30 per cent. by weight) is added and 5 c.c. of absolute alcohol to prevent frothing. The flask should be provided with a good soda trap—the ordinary Kjeldahl form is quite satisfactory. The flask is connected through a condenser to an absorption tube containing $\frac{N}{2}H_2SO_4$ coloured with methyl orange or methyl red.

At the end of 30 minutes the reaction is complete and the mixture is then raised to boiling and the solution distilled in a current of steam or a stream of air, the condenser being subsequently washed out into the absorption flasks. Stutzer and Goy [1] recommend the Devarda method for the estimation of the total nitrogen in the mixture of calcium nitrate and nitrite obtained from the arc process—but in a later publication Stutzer [2] states that the method gives low results when applied to mixtures of technical calcium nitrate and nitrolim. On the other hand, N. Buswold [3] prefers the method for the estimation

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is very much quicker than with Devarda's alloy, taking only five minutes as compared with thirty in the latter estimation. It is therefore advantageous for routine analyses where rapidity is an important factor.

A criticism of the method is given by Seydel and Wickers,[1] who state that the method is liable to give high results in the presence of much organic matter. It is useful, however, for the estimation of most commercial nitrates and nitric acids. The normal method of carrying out the estimation is as follows :—

About 0·5 gram of the nitrate, dissolved in 10–15 c.c. of water, is placed in a flask of 500–700 c.c. capacity provided with a Kjeldahl soda trap; 10 c.c. of sulphuric acid, containing about 50 per cent. H_2SO_4 are then added, and 5 grams commercial reduced iron. The flask is gently heated and finally brought to boiling after about five minutes. The contents of the flask are then diluted with 50 c.c. of water, made alkaline by the addition of 25 c.c. of 30 per cent. NaOH, and the ammonia distilled off in the ordinary way.

A detailed description of the method with the modification by Böchmann will be found in Lunge and Keane's *Tech. Methods of Chem. Analysis*, Vol. I, p. 311.

Pozzi-Escott Method.

Pozzi Escott[2] recommends the use of aluminium amalgam in alkaline solution for the reduction of nitrates and nitric acid. The nitrate (0·5 gram) is put in a distilling flask fitted with a soda trap, 5–6 grams of aluminium cuttings are added, and 2 c.c. of a saturated solution of mercuric chloride, and 150–200 c.c. of water. The procedure is then similar to the Devarda process. In order to decompose traces of ammoniated mercury compounds, a few c.c. of sodium hypophosphite solution are added towards the end.

Frabot[3] finds that simple reduction of nitrates by aluminium in alkaline solution yields accurate results, and considers that the amalgam recommended by Pozzi Escott introduces an unnecessary complication. Frabot gives the following particulars for reduction by aluminium :—

[1] *Zeitsch. angew. Chem.*, 1911, **43**, 2046.
[2] *Ann. Chim. anal.*, 1909, **14**, 445; *Compt. rend.*, 1909, **149**, 1380
[3] *Ann. Chim. anal.*, 1910, **15**, 219.

0·75 gram of the nitrate is placed in a distilling flask, with 6–7 grams of aluminium foil, and 50 c.c. of 36 per cent. NaOH are added. The flask is connected to absorption tubes containing $\bar{N}\cdot H_2SO_4$. The mixture is slowly warmed, and when all the aluminium is dissolved it is brought quickly to the boiling-point, and 40–50 c.c. are distilled over into the standard acid.

Kleiber [1] recommends the use of stannous chloride and iron filings in acid solution as a reducing agent, it being claimed that the reduction is very much quicker than reduction methods in alkaline solution.

Salle [2] uses a combination of zinc powder and ferrous sulphate as the reducing agent, in the presence of caustic soda solution, 0·5 gram of the nitrate, 200 c.c. of water, 5 grams zinc powder, 1–2 grams ferrous sulphate, and 50 c.c. of 36 per cent. caustic soda solution being the reacting substances. The suggestion is similar to König's method, in which a mixture of equal parts of zinc dust and reduced iron in alkaline solution are used as the reducing agent.

Frabot [3] finds that the method proposed by Salle is trustworthy.

Purvis and Courtauld [4] have examined the value of the zinc-copper couple as a reducing agent for the estimation of nitrates and find that organic matter renders the process inaccurate.

Phenolsulphonic Acid Method.

In this method, the nitrates, etc., are decomposed by sulphuric acid, containing phenol, whereby nitrophenol results. This is reduced to aminophenol by zinc dust, and the aminophenol estimated by the usual sulphate method. The method does not find considerable application for the general analyses under consideration in this work, however.

Titanium Method.[5]

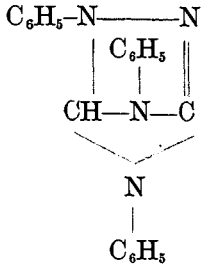
Nitrates are reduced to ammonia quantitatively and almost instantaneously by titanium hydroxide. Nitric acid or nitrate

[1] *Zeitsch. angew. Chem.*, 1909, **22**, 1363.
[2] *Ann. Chim. anal.*, 1910, **15**, 103.
[3] *Ann. Chim. anal.*, 1910, **15**, 219.
[4] *Proc. Camb. Phil. Soc.*, 1908, **14**, 441.
[5] Knecht, *J. Soc. Chem. Ind.*, 1915, **34**, 126.

equivalent to 0·1 gram KNO_3 is treated with excess of caustic soda solution (20 per cent. NaOH) and 20 c.c. of commercial titanium sulphate or chloride are added. The distillation is at once proceeded with, and after 15 minutes boiling the operation is finished and the back titration of the acid absorbent may be effected. The method is quite accurate and reliable, and is particularly useful in the assay of commercial sodium nitrate.[1]

Gravimetric Methods

The gravimetric estimation of nitric acid by nitron [2] has been the subject of a considerable amount of investigation in recent years. Nitron is 1 : 4 diphenyl—3 : 5 —*endo*-anilo—4 : 5—dihydro—1 : 2 : 4—triazole, $C_{20}H_{16}N_4$.



It forms an insoluble nitrate with nitric acid. The method of procedure recommended by Busch[3] in estimating nitric acid in solution is as follows:—

One gram of nitron is dissolved in 10 c.c. of 5 per cent. acetic acid, and the solution filtered and placed in a dark bottle. To the solution, containing preferably not more than 0·10–0·15 gram of nitrate, diluted to about 80 c.c. with water, 12–15 drops of sulphuric acid (2 parts H_2SO_4, 3 parts H_2O) are added, the liquid heated to boiling-point, and 10–12 c.c. of the nitron solution added, stirred, and allowed to stand for ½–¾ hour. Long needles of "nitron" nitrate separate on cooling. The beaker is placed in ice water for 1½–2 hours, and the crystals filtered through a Gooch crucible, using slight suction. Part of the filtrate is used for washing out the beaker. The precipitate is washed with a total of 10 c.c. of

[1] See monograph by Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*.

[2] Busch, *Ber.*, 1905, **38**, 861. [3] *l.c.*

ice water in 2 c.c. portions and dried at 105° C. for 1 hour, and then weighed.

Various substances interfere with the estimation, e.g. nitrous acid, hydrobromic, hydriodic, chromic, chloric, perchloric, thiocyanic, hydroferro and ferricyanic, picric and oxalic acids. Cope and Barab [1] give an account of detailed investigations of the method, which they consider to be very

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sulphate titration is carried out too soon, results as high as 10 per cent. in excess may be obtained, possibly owing to the formation of nitrosyl iodide, which decomposes slowly into nitric oxide and iodine. Erwin, Rupp and Lehman [1] describe a somewhat similar method in which the nitrite is oxidized by freshly liberated bromine, and the excess of bromine estimated by the addition of potassium iodide and titration with sodium thiosulphate. Dey and Sen [2] point out that the action of hydrazine sulphate on a nitrite offers a means of estimating nitrogen in nitrites. The reactions are :—

$$N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O$$
$$N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O,$$

the volume of nitrogen evolved being always two-thirds of that contained in the nitrite. Sanin [3] suggests a method based on the change of acidity occurring in the solution when a nitrite is treated with hydroxylamine hydrochloride.

$$NaNO_2 + NH_2{\cdot}OH,HCl = NaCl + 2H_2O + N_2O.$$

The hydroxylamine hydrochloride containing approximately 10 grams per litre is titrated against $\frac{N}{20}$-NaOH, using phenolphthalein as indicator; 20 c.c. of a nitrite solution containing 0·1 gram nitrite, and 20 c.c. of the hydroxylamine hydrochloride solution, are heated for 8–10 minutes on a gauze until no further bubbles of nitrous oxide are evolved on shaking. A temperature of 70°–80° C. is sufficient. After cooling, the solution is titrated with $\frac{N}{20}$ NaOH. The method is not affected by the presence of large proportions of nitrates.

Millerr [4] suggests a method for the estimation of nitrites, depending on the formation of *p*-nitroso-dimethylaniline by the action of nitrous acid on dimethylaniline hydrochloride. The method is colorimetric, and is chiefly useful for the estimation of small quantities of nitrites in water. Vanino and Schirmer [5] propose a method of estimation based on the reaction between formaldehyde and nitrous acid.

$$4HNO_2 + 3H{\cdot}CHO = 3CO_2 + 5H_2O + 2N_2.$$

[1] *Arch. Pharm.*, 1911, **249**, 214. [2] *Zeitsch. anorg. Chem.*, 1911, **171**, 236.
[3] *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 791.
[4] *Zeitsch. angew. Chem.*, 1913, **26**, 3.
[5] *Zeitsch. angew. Chem.*, 1913, **26**, 651.

The nitrogen is collected over caustic potash, and measured, with the usual precautions.

Maderna and Coffetti [1] propose to estimate nitrites in the ordinary nitrometer apparatus. When a solution of a nitrite is treated with potassium ferrocyanide solution in the presence of acetic, oxalic, tartaric, or citric acids, nitric oxide is evolved. The advantages claimed for the process are :—

1. The volume of gas is easily read.
2. Method can be applied to strong solutions.
3. No strong acids are used.

There are, however, obvious sources of error in the method due to the solubility of NO in the aqueous solutions. Furthermore, if acetic acid is used, the vapour tension will have a considerable influence on the ultimate reading of the gas volume. The reaction is :—

$$K_4Fe(CN)_6 + KNO_2 + 2CH_3COOH = K_3Fe(CN)_6 + 2CH_3COOK + NO + H_2O.$$

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They apply their method to the estimation of nitrous acid in mixed acids containing organic matter (e.g. oxalic acid), where the permanganate method for nitrites is not available (see p. 360). A convenient method of procedure is as follows :—

2·5–3·0 grams of the mixed acid, containing approximately 5 per cent. of nitrous acid and 80 per cent. H_2SO_4, are weighed out into a nitrometer and washed in with 10–15 c.c. of an aqueous solution of potassium citrate (40 per cent. by weight), 5 c.c. of a saturated solution of potassium ferrocyanide are then added and the liberation and measurement of the nitric oxide carried out in the usual way.

Fischer and Steinbach [2] describe details of a method for the estimation of nitric acid in the presence of nitrous acid, by the rapid esterification of the nitrous acid, in which oxidation to nitric acid does not take place. A mixture of sulphuric acid and methyl alcohol is made, and the mixture of nitric and nitrous acid to be tested is mixed with a little methyl alcohol, and added drop by drop to the sulphuric acid mixture, air being drawn through the solution the whole time. The

[1] *Gazzetta*, 1907, **37** (i.), 595 ; see also *J. Soc. Chem. Ind.*, 1907, **26**, 1008.
[2] *Zeitsch. anorg. Chem.*, 1912, **78**, 134.

contents of the flask are finally washed into a distilling flask and the total nitrogen estimated by the Devarda method.

The method is, however, not nearly so advantageous as the Bowman and Scott and permanganate method of estimating the mixture.

Coade and Werner [1] propose to estimate nitrites by means of thiocarbamide in acid solution. If a weakly ionized acid such as acetic acid is present, the change takes place almost completely according to the equation

$$(a)\ CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O,$$

while if hydrochloric acid is present the change is in agreement with the equation

$$(b)\ 2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O.$$

In reaction (*a*) a small quantity of nitric oxide is evolved and in (*b*) a small quantity of nitrogen, but this does not affect the estimation since the volume of gas evolved is the same in each reaction. The volume of gas evolved is measured in a nitrometer tube. The advantages claimed for the method are :—

1. The accuracy is not affected by the presence of nitrates even in large excess.

2. The analysis can be completed in a few minutes, since no subsequent manipulation of the evolved gas is necessary.

3. The volume of gas evolved can be read off with accuracy, since the operation is clean, the mercury being untarnished even after a large number of analyses.

Methods available for the Analysis of Mixtures of Nitric, Nitrous, and Sulphuric Acids

The general method of procedure is as follows [2] :—

1. Estimation of the nitrous acid by the ordinary permanganate method, using Lunge's modification.

2. Determination of the total acidity by titration with standard alkali.

3. Determination of the total nitrogen acids by nitrometer.

There are a number of alternative methods of procedure, some of which are, in the author's opinion, preferable to the above.

With regard to the estimation of nitrous acid, the per-

[1] *Chem. Soc. Trans.*, 1913, 1221.

[2] Lunge and Berl, *Zeitsch. angew. Chem.*, 1905, **18**, 1681.

manganate method is the simplest, although the method of Coffetti and Maderna [1] gives accurate results with mixed acids and is very rapidly carried out.

As an alternative to the nitrometer method for determining the total nitrogen acids, the real nitric acid is preferably estimated by the Bowman and Scott ferrous sulphate method, and the sulphuric acid then determined by difference, from a total-acidity titration. As an additional check the sulphuric acid should be determined in several samples by precipitation as barium sulphate. The method of estimating the nitrogen acids by evaporation from the mixture is not recommended by Lunge and Berl [2] owing to the difficulty of removing the last traces of nitrous acid without loss of sulphur trioxide. In mixed acids containing an excess of free nitric acid, however, the author has found this method to be fairly accurate. Finch [3] suggests the following method of operation:—

The total acidity of the mixed acid is determined with a decinormal solution of barium hydrate, using phenolphthalein as indicator. The solution is then heated to boiling, and the barium sulphate filtered off and washed free from soluble barium salts. The filtrate and washings are then heated to boiling-point and titrated with neutral $\frac{N}{5}K_2CrO_4$ $\left(\begin{matrix}\text{free from}\\ CO_2\end{matrix}\right)$ until a permanent yellow coloration is obtained. The titration must be carried out in a hot solution, and the chromate run in very slowly. It is necessary to filter off the barium sulphate, since it reacts appreciably with potassium chromate. The nitrite is determined in the original solution by the ordinary permanganate method. The reactions taking place are as follows:—

1. $H_2SO_4 + 2HNO_3 + 2OH{\cdot}SO_2{\cdot}ONO + 5Ba(OH)_2 = 3BaSO_4 + Ba(NO_3)_2 + Ba(NO_2)_2 + 8H_2O.$

2. $Ba(NO_3)_2 + Ba(NO_2)_2 + 2K_2CrO_4 = 2BaCrO_4 + 2KNO_3 + 2KNO_2.$

Similar methods of estimation to those previously described are also recommended for the analysis of spent acid from the manufacture of nitroglycerin by Lemaitre.[4]

[1] *l.c.* [2] *l.c.* [3] *Schiess und Sprengstoff.*, 1912, **7**, 113, 387.
[4] *Mon. Scientif.*, 1907, **21**, 809.

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